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Commercial utilization of lignin

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NOTE TO USERS

COMMERCIAL UTILIZATION OF LIGNIN

by

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I. INTRODUCTION

Lignin is found throughout the plant world in vast quantities. Second only to cellulose in abundance as a natural vegetable product (41) lignin is produced year after year as new plants come into existence and reach maturity.

Cellulose and lignin together with the hemicelluloses constitute the principal organic materials in all plants. It is widely believed that the cellulose serves as the structural or strength giving unit to plant materials, while the lignin acts as a binding or filling material for the plant cells, thus providing rigidity to the cell wall. The hemicelluloses appear to function principally as a reserve food material.

The largest isolated source of lignin available today is in the effluent waste liquors from the pulp and paper mills of this country. Conservative estimates (66) place the supply from the sulfite pulping process alone at some 1,500,000 tons per year. To be added to this quantity are some 1,300,000 tons of alkali lignin from the soda and sulfate pulping processes which are now burned for subsequent recovery of the soda (86). Small, however, are these when compared to the potential supply, as yet untapped, from agricultural residues remaining after crop harvests. It has been estimated (7) that the average annual production of plant residues is over 1,000,000,000 tons. With lignin constituting some 15 to 25 per cent of these materials, this latter source, based on an average value, indicates a supply of approximately 200,000,000 tons per year of lignin. Making up the larger part of the preceding figures are straws, leaves, cobs, hulls, stalks and bagasse, all of which are easily collected. An estimate by Jahn of the New York

State College of Forestry (86) places the amount of lignin available annually from the logging, sawmilling, and wood-working industries as over 15,000,000 tons in sawdust, shavings, and other forms of wood waste.

The critical problem, however, deals with the lignin produced in the pulp and paper mills (137) and other sources, such as the residue from the furfural process from oat hulls. In many localities, legislative action now prevents effluent waste sulfite liquor discharge into the rivers and streams. Thus, today lignin occupies a position quite similar to that of coal tar during the middle of the past century. Then coal tar was a waste material in the production of coke for the blast furnace and its disposal was a serious problem. Today lignin is a waste material in the production of cellulose for the paper and allied industries and its disposal, likewise, is a matter of prime importance. The problem of eliminating a nuisance in the case of coal tar occasioned much of the research which has resulted in the host of valuable aromatic materials that are used in every walk of life. Perhaps the time will come when lignin itself will be the parent substance for an important group of valuable materials.

Recent developments have shown that lignin can be separated economically from the discharged waste pulping liquors of both major pulping processes, namely, the soda (125) and sulfite (82)(137). However, more to the point, late research shows that this recovered lignin can be utilized satisfactorily. It can be used in the plastic field, as a plasticizing agent in concrete, and as a source of vanillin and many valuable phenolic materials. These and others, unfortunately, utilize only a minute fraction of the lignin available. From the preceding, it is seen that lignin can serve as a basic

raw material. In addition, it is widely distributed on the earth's surface, wherever climate and environment are suitable for plant growth.

Any commercial utilization of lignin, to be significant, requires the consumption of vast quantities. With this point in mind, a series of investigations was commenced in an effort to find promising uses for lignin. Among the projects studied were: the production of azo dyes (149)(155)(23), vanillin (133)(23), plastics (87), base-exchange materials for water softening, and the degredation or cleavage products of lignin resulting from nitration (105), chlorination (87)(255), caustic fusion (139), and ammoniation (155). Of these, the production of vanillin and the production of a base-exchange material for water softening appeared to be promising. As a result, this thesis has had as its principal objectives, first, the development of base-exchange materials from lignin to be used in water treatment and, second, a study of the alkaline nitrobenzene treatment of the oat hull furfural residue as a source of vanillin.

II. PROPERTIES OF LIGNIN

More than 100 years have passed since lignin was first recognized as a constituent of plant material, but despite much intensive investigation its structure still remains obscure. This is principally due to the fact that lignin does not readily split up into identifiable building units.

Schulze (132) is generally credited with having introduced the term lignin into the chemical literature. Payen (115), however, was the first to recognize the existence of such a substance as a component of plant material. Payen discovered that woody materials could be separated into two fractions by treatment with nitric acid followed by a digestion with potassium hydroxide. The substance that was removed Payen called "incrusting materials." He found that the insoluble portion, principally cellulose, contained a lower percentage of carbon than did the soluble fraction removed from the wood.

Much remains to be learned about the exact structural relationship of the various component parts of the nucleus of the lignin molecule. Recent work, however, indicates that the nucleus is definitely aromatic in nature. The reactive groups located on the nucleus have recently been identified and classified, both as to type and as to the number of each type.

Lignin is a body of very high molecular weight. This is not at all surprising, since the basic lignin building unit itself is of high formula weight, somewhere in the neighborhood of 850 (18).

Lignin from one particular plant may differ somewhat from lignin from another source. In addition, differences in composition are often noticed

for lignin from the same source when isolated by different methods. As a matter of fact, it has not been established that lignin from a given plant is one chemical compound. It has been noticed, however, that lignins from different sources and isolated by various methods have many reactions in common and are alike in many respects. In any event, they may be treated similarly, at least qualitatively.

A. Occurrence of Lignin within the Plant

In the plant lignin is found principally in two places. In one it appears to be combined chemically with cellulose as a lignocellulose in the walls of the plant cells, while in the other a somewhat smaller amount is deposited in the middle lamella between the plant cells apparently in an uncombined form. In addition, a small amount of lignin is combined with the hemicelluloses also present in the plant cell.

To date no complete agreement has been reached among lignin research workers as to the type of linkage by which lignin is combined with cellulose. In fact, in some cases it even appears that the cellulose is only mechanically impregnated with lignin. Supporters of this hypothesis, the so-called "incrustation hypothesis," are König (92), Wislinceanus (158), and more recently Freudenberg (42). The majority of the facts, however, support chemical combination of one type linkage or another. Erdman (31) arrived at the conclusion that an ester-like union exists between an acidic group in the lignin and a hydroxyl group of the cellulose. Mehta (106) advanced the view that an ether-like linkage occurs between lignin and cellulose. Holmberg (79) suggests that the lignin in wood is combined with the

carbohydrates in acetal-like manner. Phillips (120), while working with corn cobs, found that the lignin seems to be dissimilarly combined; part possibly in the form of an ester, while the remainder is more firmly held, such as would be the case in an ether type of linkage. To further substantiate the view of chemical combination with the carbohydrate materials, Harris (66) points out that there is no example known where lignin has been isolated without the application of hydrolytic reactions. Such a hydrolytic action would result in breaking the ester, ether, or other type of linkage. Common materials bringing about this hydrolytic action are: sulfuric acid (134); hydrochloric (157) and other mineral acids (154); organic acids (111); pulping chemicals (65); bases (119); fungi (33) or hydrolytic enzymes present in wood (34).

B. Constitution of Lignin

1. Chemical composition, molecular weight, and physical properties

Lignin may be defined as the noncarbohydrate portion of the extractive free plant tissue. In general, it contains approximately 60 to 65 per cent carbon and 5 to 8 per cent hydrogen (19), whereas carbohydrate materials analyze about 45 per cent carbon and 6 per cent hydrogen.

A number of investigators have done work on the molecular weight of lignin (67)(18)(53)(19). Their results indicate a unit molecular weight near 850. Hibbert and co-workers (19) believe that this unit of a molecular weight of about 850 is characterized by the presence of one phenolic and one enolic group and they refer to it as the "lignin building unit." Recently a new term has crept into lignin chemistry, namely, "lignin

building stone." This latter has a molecular size of only about 170 and refers to a C6-C3 group. Five of the "lignin building stones" thus make up one of the "lignin building units," in the same manner that glucose is the building stone of cellulose and starch, and cellobiose and maltose are their respective building units (18). Molecular weight studies of methanol lignin in solution in organic solvents indicate a molecular weight of between 4,000 and 10,000 for lignin separated in this manner (103).

Many empirical formulas have been suggested for lignin. Brauns (18) presents a formula of $C_{47}H_{52}O_{16}$ for methanol lignin from spruce wood. Harris (66) gives a formula of $C_{48}H_{52}O_{18}$ for maple wood lignin isolated by the 70 per cent sulfuric acid method.

Lignin ranges in color from a light yellow through a dark brown to a deep black, depending largely upon the method of isolation. It is isolated as an amorphous powder. Lignin from the sulfite pulping process, which is ordinarily obtained as a calcium lignosulfonate, is soluble in water and alkali, but is only very slightly soluble in organic solvents. On the other hand, lignin separated by the alkali process, which is a sodium lignate, is soluble in many organic solvents.

Lignin from practically all sources fuses on heating, with the fusion temperature and point at which thermal decomposition sets in extremely close together. Generally, free lignin molded without condensing agents or plasticizers gives a very brittle product of low mechanical strength, although a very smooth hard surface can be obtained.

2. Reactive groups in the lignin molecule

For many years it has been recognized that lignin possesses certain definite reactive groups. The recent work of Harris (66) summarizes the

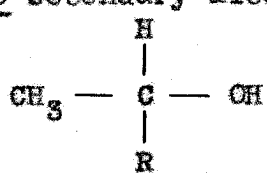
present knowledge of this phase of lignin chemistry. Working with maple wood lignin isolated with 70 per cent sulfuric acid from completely extracted green wood, he identified and classified the reactive groups of the lignin molecular building unit, largely through chlorination and methylation studies. Table 1, shown below, provides information regarding the reactive groups found to be present in the lignin building unit. The material used analyzed

CH_3O	20.8%
C	63.3%
H	5.7%

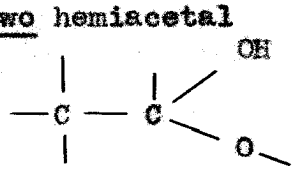
Table 1

Four Hydroxyl Groups

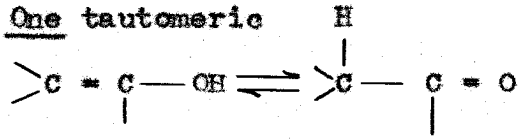
1. One secondary alcohol



2. Two hemiacetal



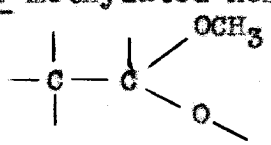
3. One tautomeric



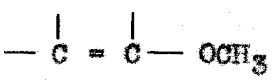
4. Two double bonds

Six Methoxyl Groups

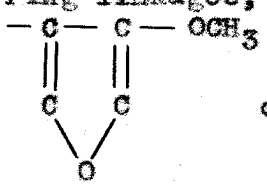
5. One methylated hemiacetal



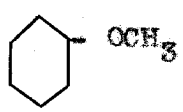
6. One methylated enolic



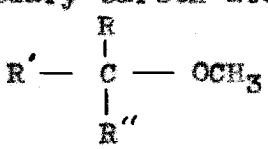
7. Three methoxyls attached to ring linkages, such as



or



8. One methoxyl attached to a tertiary carbon atom



Calculated on the basis of these reactive groups the apparent formula weight for this lignin building unit is about 910. As is shown in Table 1, the presence of six methoxyl groups, four hydroxyl groups, and two ethylenic double bonds is indicated. This corresponds to an empirical formula of

$$C_{42}H_{30}O_8(OCH_3)_6(OH)_4$$

for the lignin building unit. Eight oxygens are unidentified. They appear to exist in ether linkages, lactone rings, or as a part of a ring such as furan.

Harris points out that the one tautomeric group, No. 3 in Table 1, apparently is responsible for most of the characteristic reactions of lignin. The solubility of lignin in alkali is due to this group. Methylation with diazomethane stabilizes the enol configuration and the lignin no longer is soluble in alkali. In addition, it no longer shows the reactions of a keto form, a typical example of which is the wine red coloration with phloroglucinol. In an earlier work (67) Harris and co-workers indicated that isolated lignin appears to exist principally in the keto form, while the original lignin in the plant is in the enolic form and is combined with the carbohydrate materials.

The fact that lignin forms stable lignosulfonic acids by the addition of acid sulfites is believed due to the presence of two ethylenic linkages, No. 4 in Table 1. Thus, it appears that there can be two sulfonic acid groups attached to each lignin building unit of a formula weight of about 900. This reactive linkage, then, apparently is largely responsible for the success of the sulfite paper pulping process.

Brauns (18) in working with spruce wood lignin extracted with methanol and hydrochloric acid identified the following groups.

$$C_{41}H_{31}O_6(\geq C = O)(OCH_3)_4\ (OH)_4$$

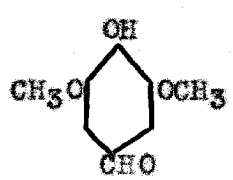
It will be noted that this is in close agreement with the empirical formula submitted by Harris (66), mentioned previously, of

$$C_{42}H_{30}O_8(OCH_3)_6\ (OH)_4$$

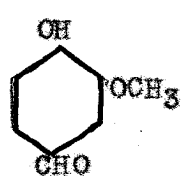
The principal difference between lignin from various sources and isolated by different methods appears to be in the methoxyl content. Otherwise the characteristic reactions are much the same. As is pointed out in Table 1, the methoxyl groups are attached to either ring linkages directly or to certain reactive aliphatic groups. Methoxyl groups attached directly to an aromatic nucleus are firmly held and thus not so easily cleaved. On the other hand, those not bound to an aromatic structure are more easily removed. Differences in treatment during the separational step could easily bring about cleavage of the methoxyl groups from the reactive groups in varying amounts, such as No. 5, 6, and 8 in Table 1. This fact, then, could account for a variation in the methoxyl content for lignin from the same source when isolated under different conditions.

Hibbert and co-workers (71), utilizing a new method of lignin degradation, found that the ratio of syringaldehyde to vanillin in lignin from different plant materials varied considerably.

Syringaldehyde



Vanillin



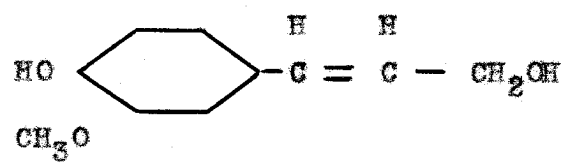
It appears that the variation in the methoxyl content of lignin from different woody substances may be accounted for partly in this way. As a result of the high yields of vanillin and syringaldehyde obtained, Hibbert has postulated that alpha-hydroxypropiovanillone and alpha-hydroxypropiosyringone are the parent materials and that they condense together with a loss of water to form lignin.

3. Structure of the lignin nucleus

Much disagreement is to be found in the literature concerning the structure of the lignin nucleus. In general, the principal differences of opinion may usually be classified into either of two groups. The first believes that lignin is of aromatic nature and exists as such in the plant, while the second feels that lignin is of carbohydrate origin and is the result of a secondary reaction brought about in the separational step. Hilpert (75) may be regarded as a supporter of this latter contention. It should be pointed out here that the great majority of lignin chemists now feel that a large part of the lignin molecule is of aromatic structure and exists as such in the plant. Recent work (48)(71) tends to establish this conclusion almost without doubt.

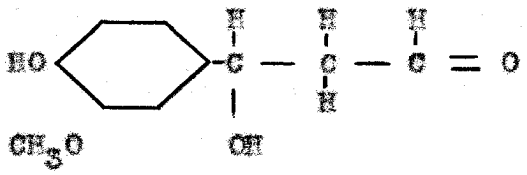
As early as 1897 Klason pointed out the close relationship between lignin and coniferin, the glucoside of coniferyl alcohol, an aromatic alcohol.

Coniferyl Alcohol



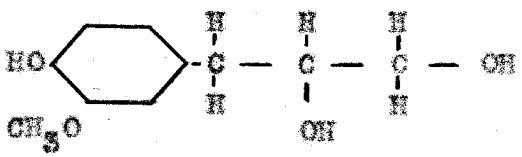
Later Klason (80) revised his original formulation and suggested that coniferyl aldehyde appears to be the basic building stone in lignin.

Coniferyl Aldehyde

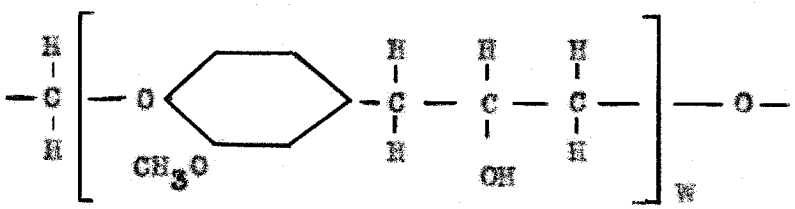


In 1933 Freudenberg (47) proposed that 2, 3-dihydroxypropyl guaiacol and its derivatives are the building stones of lignin.

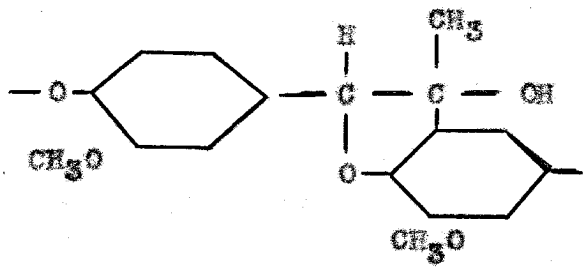
2, 3-Dihydroxypropyl guaiacol



An early theory regarding the structural relationship of the lignin building stones, presented by Freudenberg (43), assumed that the primary hydroxyl is joined through an ether linkage with one of the phenol hydroxyls of the next molecule and a condensation product is formed.



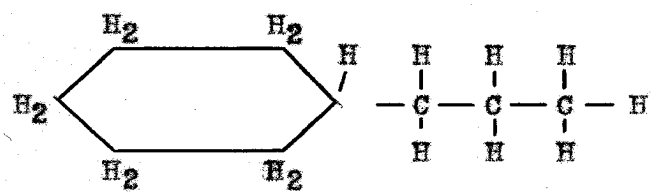
Shortly afterward Freudenberg (47) abandoned the above theory concerning the structure of lignin and he suggested that the union to form lignin may take place as indicated below.



Despite the fact that these formulas are to a considerable extent speculative, it appears that Freudenberg has provided more facts than any other investigator (52) to verify his contentions regarding a structural formula for lignin. It might be pointed out that Freudenberg's conclusions are not entirely in agreement with the recent work of Harris (66) on the reactive groups present in the lignin molecule, although there are many points in which there is close similarity of opinion.

Recently (66) Harris obtained yields of approximately 50 per cent of n-propylcyclohexane and its derivatives by the hydrogenation of lignin.

n-propylcyclohexane

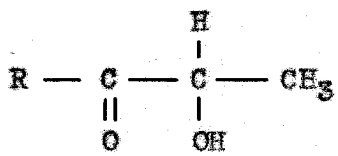


Although the hydroxyl and methoxyl groups have been removed in the above treatment, nevertheless it is a very important contribution in that it shows that a large part of the lignin molecule is built up of the C6-C3 building stones.

The above evidence, coupled with the work of Freudenberg (48) and Hibbert (71) in which yields of over 50 per cent of vanillin, syringaldehyde, and their derivatives were obtained, definitely establishes the presence of an aromatic nucleus with a three carbon side chain. Additional evidence favoring the presence of an aromatic nucleus in the lignin molecule is the fact that substantial amounts of aromatic substances are formed in the alkali fusion of lignin as shown by Heuser and Herman (70). Catechol and protocatechuic acid in nearly 25 per cent yield were obtained.

Based on these late developments in the knowledge of lignin chemistry

Hibbert (71) has very recently proposed that the building stones in lignin are alpha-hydroxypropiovanillone and alpha-hydroxylpropiosyringone. They condense together in varying ratios with the elimination of water to form lignin.



"R" may be either the syringyl or the guaiacyl groups.

Studies on the absorption spectra of lignin and lignin derivatives by Herzog and Hillmer (69) indicate a benzenoid structure for lignin.

In any event, it will be noted that C6-C3 group appears to be fundamental in the lignin molecule and, as mentioned earlier, five of these C6-C3 "lignin building stones" form a "lignin building unit" having a formula weight of about 850.

C. Chemical Reactions of Lignin

Lignin is a very reactive material. When treated under mild conditions the reactions taking place are largely those of the reactive aliphatic side chain groupings, but when more drastic treatment is used a complete disruption of the nucleus takes place.

In the case of oxidation, lignin is especially reactive. In fact, even mild inorganic oxidizing agents will completely disrupt the molecule giving simple degradation products. Formic and oxalic acids have been obtained from the action of ozone on lignin. Hydrogen peroxide in neutral and in alkaline solutions yields simple organic acids, such as formic,

acetic, oxalic, succinic and malonic acids. Mild organic oxidizing agents, such as nitrobenzene, are especially valuable in degrading lignin. With this latter oxidizing agent the intermediate products formed, such as vanillin, are not oxidized further. Strong oxidizing agents, e.g., nitric acid, give oxalic acid as the chief product.

Lignin may be nitrated very readily with nitric acid or with mixed acid. The product obtained is usually an orange brown amorphous powder. The nitrogen introduced into the lignin molecule is present as both ester (NO_3), nitro (NO_2) and nitroso (NO) nitrogen. In other words, nitration has proceeded with the aliphatic side chain hydroxyls, in addition to direct nitration of the aromatic nucleus. Nitrated lignin may be reduced to give aromatic amine groups (72). Degradation products such as the various dinitrophenols and even picric acid have been obtained.

Fusion with alkali at elevated temperatures has resulted in the formation of aromatic and simple aliphatic compounds. In nearly all cases the reaction products identified have been vanillic acid, protocatechuic acid, catechol, oxalic, acetic acids and other simple aliphatic compounds. Below 240° C. the principal material obtained is a dark, amorphous degradation product, generally referred to as "lignic acid." Hydrolysis of lignin with dilute sodium hydroxide at somewhat lower temperatures results in the formation of small amounts of vanillin. When aromatic products are obtained, the action taking place apparently is one involving breakage of the carbon-carbon aliphatic side chain. Care must be taken to exclude atmospheric oxygen if it is desired to retain the aromatic degradation products.

Lignin may be hydrogenated by any of several methods. Direct high pressure catalytic hydrogenation can convert lignin completely into liquid and gaseous products, of which methanol and derivatives of n-propyl-

cyclohexane have been the principal products identified. Hydriodic acid and red phosphorous react with lignin at elevated temperatures to give high yields of hydrocarbons together with some oxygen containing substances of an acidic nature. When lignin is distilled with zinc dust in an atmosphere of hydrogen, good yields of aromatic phenolic materials are obtained, such as 1-n-propyl-3-methoxy-4-hydroxybenzene, guaicol and similar phenolic derivatives.

Bridger (21), in work conducted in this laboratory, found that the dry or destructive distillation of lignin is an excellent method for obtaining many phenolic materials. By carefully controlled fractionation of the liquid tar, the following materials were obtained and identified: phenol, o-cresol, p-cresol, guaiacol, 3,5-xylenol and cresol. On the basis of the lignin tar the yield of each varied generally between 5 and 10 per cent. Since conditions are extreme in the case of the destructive distillation, it is apparent that a complete disruption of the lignin molecule takes place. The high stability of the benzene nucleus at elevated temperatures accounts for the large amount of phenolic materials present. Other materials obtained in the destructive distillation of lignin are methanol, acetic acid and acetone. As a matter of fact, in the wood distillation industry, it is the lignin present in the wood that is largely responsible for the methyl alcohol produced.

Lignin undergoes sulfonation quite readily. The stability of the lignosulfonic acids formed by the addition of the alkaline earth acid sulfites indicates a strong carbon-sulfur linkage, such as would be the case when addition to an ethylene double bond takes place. This type of reaction may be recognized as that taking place in the sulfite paper pulp-

ing process. Lignin may also be sulfonated directly with concentrated sulfuric acid. It appears that sulfonation of the aromatic nucleus takes place as distinguished from the preceding type of sulfonation which is apparently additional to an ethylenic double bond.

Lignin is extremely reactive with chlorine. The majority of its reactions are with the reactive aliphatic side chains; however, chlorine will also substitute into the aromatic nuclei when suitable catalysts, such as ferric chloride are present. As was pointed out in the section on the reactive groups present in the lignin molecule, chlorination has been especially important in aiding in the identification of these groups. Reaction may take place by either addition or substitution. Among the compounds that are split out are: hydrochloric acid, methyl alcohol, chloroform and many similar chlorinated derivatives. Derivatives of lignin itself, containing as much as 45 per cent of chlorine, have been obtained. Other halogens are equally reactive with lignin.

Lignin acetylates easily. Acetic anhydride, used in various solvents, is the most common acetylating agent. As many as three or four acetyl groups may be introduced into the lignin molecule. In this case, the reaction appears to be principally with the hydroxyl groups in the aliphatic side chains.

Alkylation of lignin with the usual alkylation agents, e.g., diazomethane, dimethyl sulfate, etc., proceeds readily. All hydroxyl groups may be methylated, the result of which is that lignin becomes insoluble in alkali. The methoxyl content of maple wood lignin has been

increased from a normal content of 20.8 per cent to a total of 32.2 per cent when methylated with dimethyl sulfate (66).

Hydrolysis is one of the few reactions to which lignin does not respond readily. This is not at all surprising, however, since the formation and separation of lignin from the carbohydrate materials present in the plant is, almost without exception, dependent upon some sort of a hydrolytic action. Hydrolysis of lignin may proceed, however, to the point whereby a large percentage of the methoxyl groups may be cleaved from the lignin molecule. This is usually carried out at elevated temperatures in the presence of small amounts of dilute acid.

For an excellent review on the reactions of lignin, the work of Phillips (122) is the most comprehensive yet to appear. A great many valuable references regarding this subject are also to be found.

D. Isolation of Lignin

Lignin and its associated materials in the plant substance, cellulose and the hemicelluloses, are separated by either of two general methods. The first removes all other materials, largely by hydrolysis, leaving the lignin behind. The second consists in dissolving the lignin, thus separating it from the cellulose. Eventually the lignin may be precipitated from the solution. This latter method of dissolving the lignin is that commonly used in the commercial pulping processes. Direct methods for the quantitative estimation of lignin also fall within these same two general classifications.

1. Quantitative estimation of lignin

The methods of the first class, that is, those that depend upon dissolving the cellulose and other carbohydrates and leaving the lignin as an insoluble residue, are most commonly employed for the quantitative estimation of lignin. Among these, the more reliable methods appear to be the 72 per cent sulfuric acid method of Klason (91) and the fuming hydrochloric acid method of Willstätter (157). Even at room temperature acids of these concentrations smoothly hydrolyze the insoluble cellulose and other components to soluble degradation products. A very commonly used modification of the Klason method is that of the United States Forest Products Laboratory (20). Billington, Simmonds, and Baird (13) in a study of methods for the determination of lignin concluded that the method of Willstätter, fuming hydrochloric acid, possesses the greatest inherent accuracy.

A method of the second class, used to some extent, is that of Mehta (106). This method is based upon the fact that the lignin fraction in lignified plant material can be removed by heating the latter with alkali under pressure. The soluble alkali lignin is then precipitated by addition of hydrochloric acid and it is subsequently purified. In general, the lignin values obtained by this method are lower than those obtained in either of the acid methods of the first class.

2. Sources of lignin

As mentioned earlier, to date there are no methods known whereby lignin can be isolated unchanged from its condition in the plant--the

claims of many investigators to the contrary. In addition, some methods are more drastic than others and thus yield a lignin material that has been degraded considerably.

For studies on lignin, where a minimum of contaminating material is desired, it is customary to first remove from the plant substance the various "extractives," such as fatty substances, resins and volatile oils. This is done by extraction with various organic solvents, preferably an alcohol-benzene mixture.

For the quantitative estimation of lignin the most important methods utilize the removal of the non-lignin material leaving an insoluble lignin residue, but the methods possessing greatest commercial importance depend upon the solution of the lignin and its subsequent precipitation for recovery. Exceptions in which lignin is obtained as a by-product are the Bergius process (11) and the Scholler-Tornesch process (61), used in Germany for the hydrolysis of cellulose to sugars and alcohol. Another process somewhat similar in nature to the latter two is that used for the production of furfural from oat hulls. The lignin, however, is highly admixed with cellulose, since only the pentosans are hydrolyzed to any great extent by the acid treatment. The residue remaining is not pure lignin, since the percentage composition of cellulose and lignin has been increased by elimination of the pentosans.

a. Sulfite lignin. The sulfite process is the most important of all the commercial pulping methods. The plant material is delignified by conversion of the lignin to a soluble lignosulfonate through action of alkaline earth acid sulfites, thus separating it from the cellulose. Waste sulfite liquors are extremely objectionable when discharged into

rivers, streams and lakes because of their toxicity and high oxygen demand. The detrimental effects of the effluent sulfite liquors on stream life have instituted much work recently on their recovery. The most common methods either evaporate the sulfite liquor or recover the lignin by precipitation as the calcium lignosulfonate. Particularly economical is the latter method as developed by Howard (84).

The Howard process consists in treating the sulfite liquors with a lime solution at regulated pH values. A flow sheet of the process is provided in Figure 1 which appears on the next page. In the first step a small amount of the lime is added until calcium sulfite precipitates. Optimum conditions are maintained for large crystal growth. The calcium sulfite is removed from the bottom of the settling tank and returned for regeneration to calcium acid sulfite by the free sulfur dioxide present in the fresh pulping liquors, thereby recovering a large amount of this material for reuse in pulping. Addition of more lime in the second precipitation tank increases the pH to the point where an insoluble basic calcium lignosulfonate is precipitated. After settling, the gelatinous precipitate is filtered on a rotary vacuum filter and then dried in a vacuum drum drier. The liquid effluent containing the soluble carbohydrates is discharged in a much less objectionable form.

The Marathon Paper Company of Rothschild, Wisconsin, holds the patent rights to the above process. At one of their mills in Wisconsin (84) the process is in full operation.

b. Soda lignin. Next in importance to the sulfite process as a source of high grade cellulose pulp is the soda process. Here, advantage is taken of the solubility of the lignin and the hemicelluloses in hot

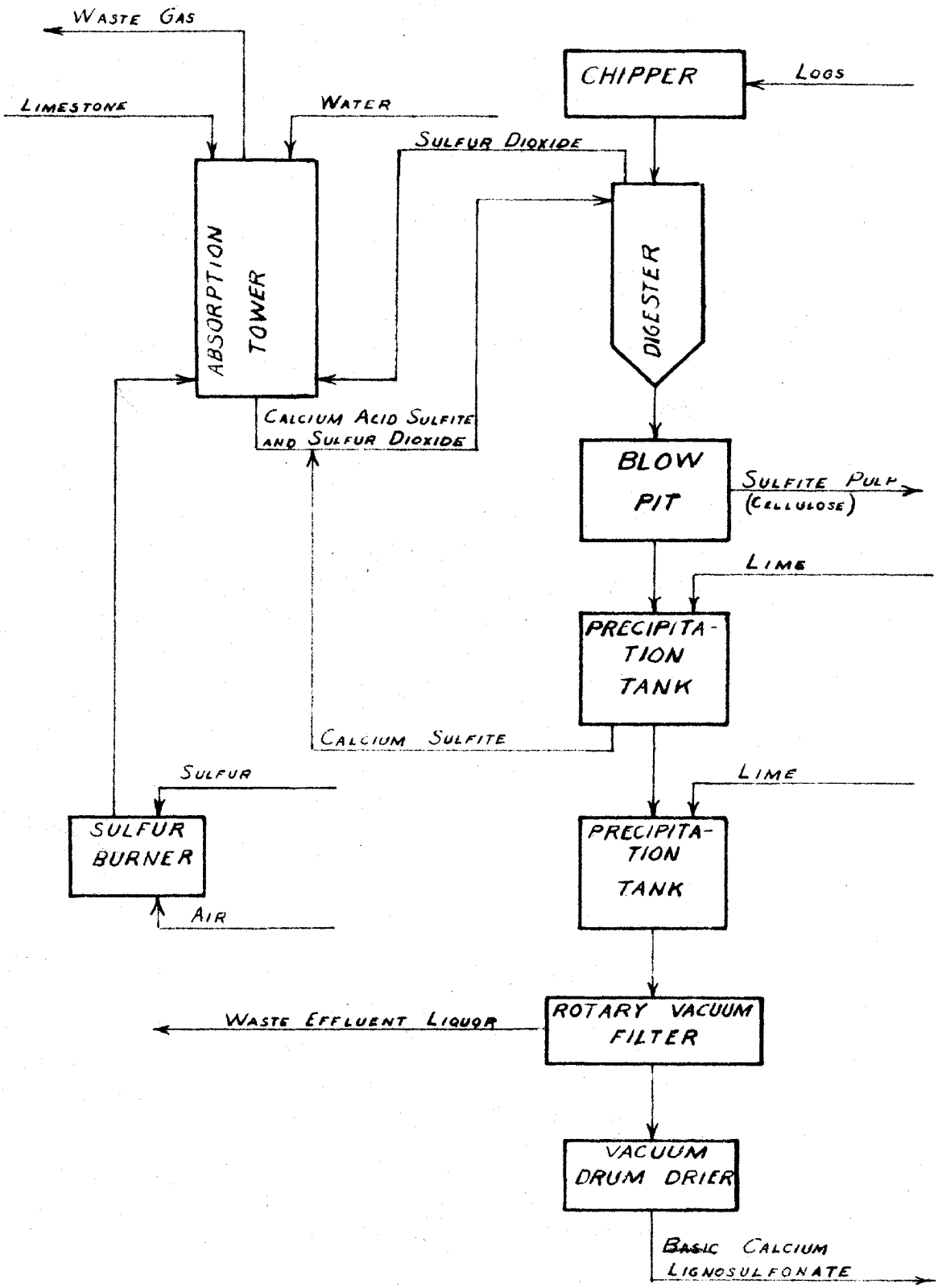


FIG. 1. PRODUCTION OF ~~BASIC~~ CALCIUM LIGNOSULFONATE FROM WOOD

dilute sodium hydroxide. The lignin is converted to a soluble sodium lignate. Acidification by any of several acids precipitates the lignin and hemicelluloses. The hemicelluloses become soluble upon heating, thus leaving the insoluble lignin in a reasonably pure state.

In the case of the sulfate process the lignin is dissolved by a mixture resulting from the reduction of sodium sulfate, consisting principally of caustic soda, sodium carbonate and sodium sulfide. Some lignin and hemicelluloses remain in the cellulose pulp. Very little has been done on the recovery of the lignin from the pulping liquors of this process.

The usual practice is to concentrate the black liquors from the soda and sulfate processes by evaporation and then to burn the lignin and other organic matter to generate by-product steam. The soda chemicals are recovered from the resulting ash for reuse in preparing new cooking liquor. The ash consists principally of sodium carbonate.

The lignin can be separated by precipitating it from the alkaline black liquors upon treatment with acid. Sulfuric, hydrochloric or any of the strong acids can be used; most economical, however, is carbon dioxide. The use of this latter material forms the basis of a new commercial process (125) for obtaining lignin. A flow sheet of the process using this method of producing lignin is shown on Figure 2. This is the process as carried out by the Meade Paper Company in producing their soda lignin product Meadol. A pilot plant is now in operation at Chillicothe, Ohio, producing about 500 pounds of Meadol per 24 hours.

c. Lignin from the saccharification of woods. Wood chips and sawdust are used as the raw materials in a process developed by Scholler at Tornesch in Germany for the production of a sugar solution to be used

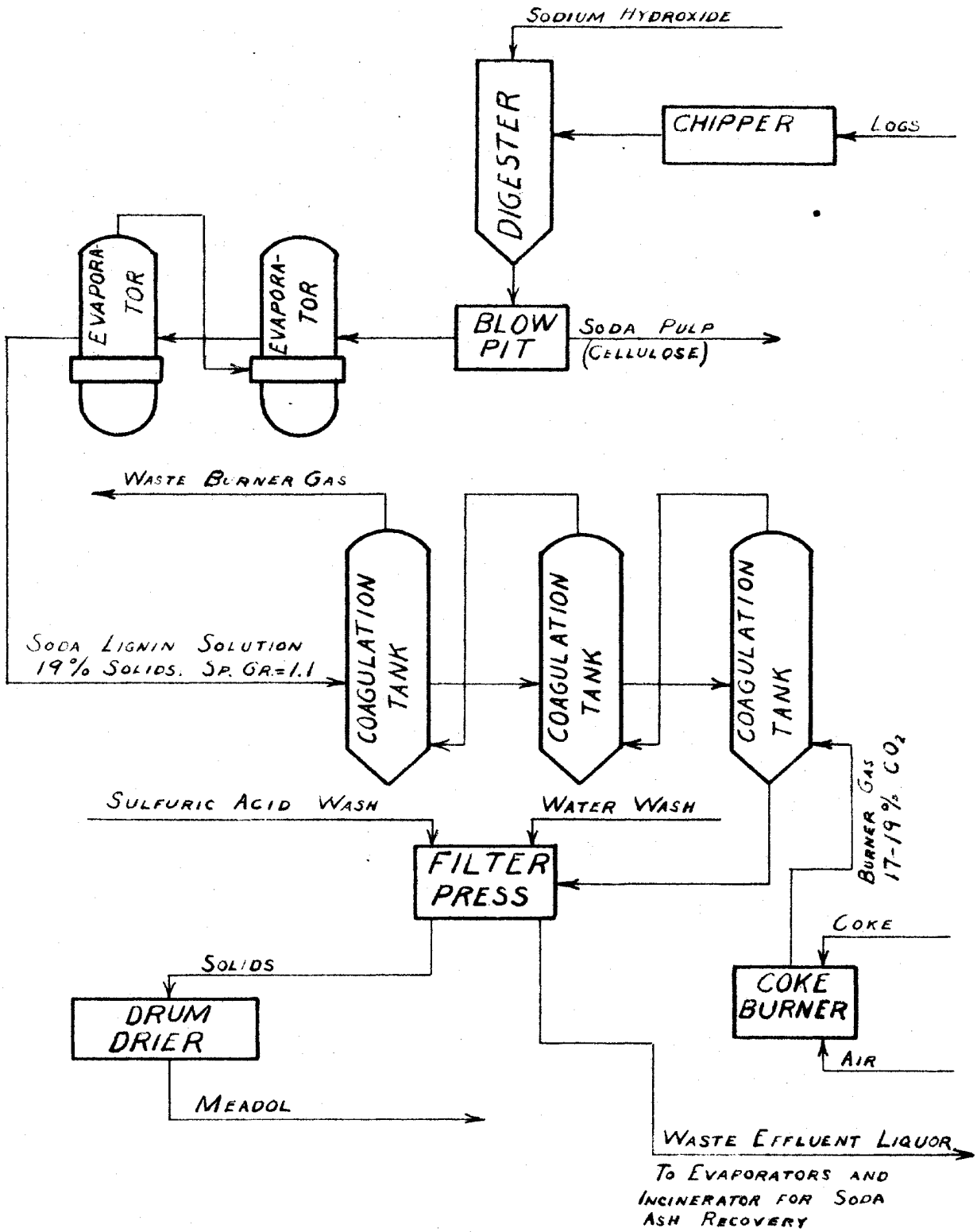


FIG. 2. PRODUCTION OF MEADOL FROM WOOD

ultimately for fermentation to ethyl alcohol. Lignin is obtained as a by-product and serves little use at present other than to provide the necessary heat for fermentation and distillation. It is quite pure, has little ash and briquettes easily. A somewhat similar process is that of Bergius (11). In this case, however, a much higher acid concentration, fuming hydrochloric acid, is used to aid hydrolysis.

Cellulose is hydrolyzed in the presence of sulfuric acid to glucose. If the glucose is not removed and cooled shortly after formation, it is partly decomposed at the necessary high temperature and pressure. Pressure percolation of the hydrolyzing acid through the wood chips and sawdust followed by its rapid cooling after passage through the percolators are the principal features of the process which are responsible for its success. A pressure of approximately 150 pounds per square inch with a temperature range of 170 to 180° C. are used.

The lignin is discharged from the bottom of the percolators as an insoluble residue, while the 0.2 to 1.2 per cent sulfuric acid solution containing the dissolved sugar is neutralized with lime and rock calcium phosphate. Yields of 48 to 55 gallons of alcohol per ton of dry wood are obtained.

A flow diagram (61) appears on the next page showing the essential features of the process.

d. Furfural oat hull residue. Although not a pure lignin, an excellent source of a material high in lignin is the oat hull residue remaining following the sulfuric acid and steam treatment of oat hulls in the production of furfural. The elimination of the pentosans present to

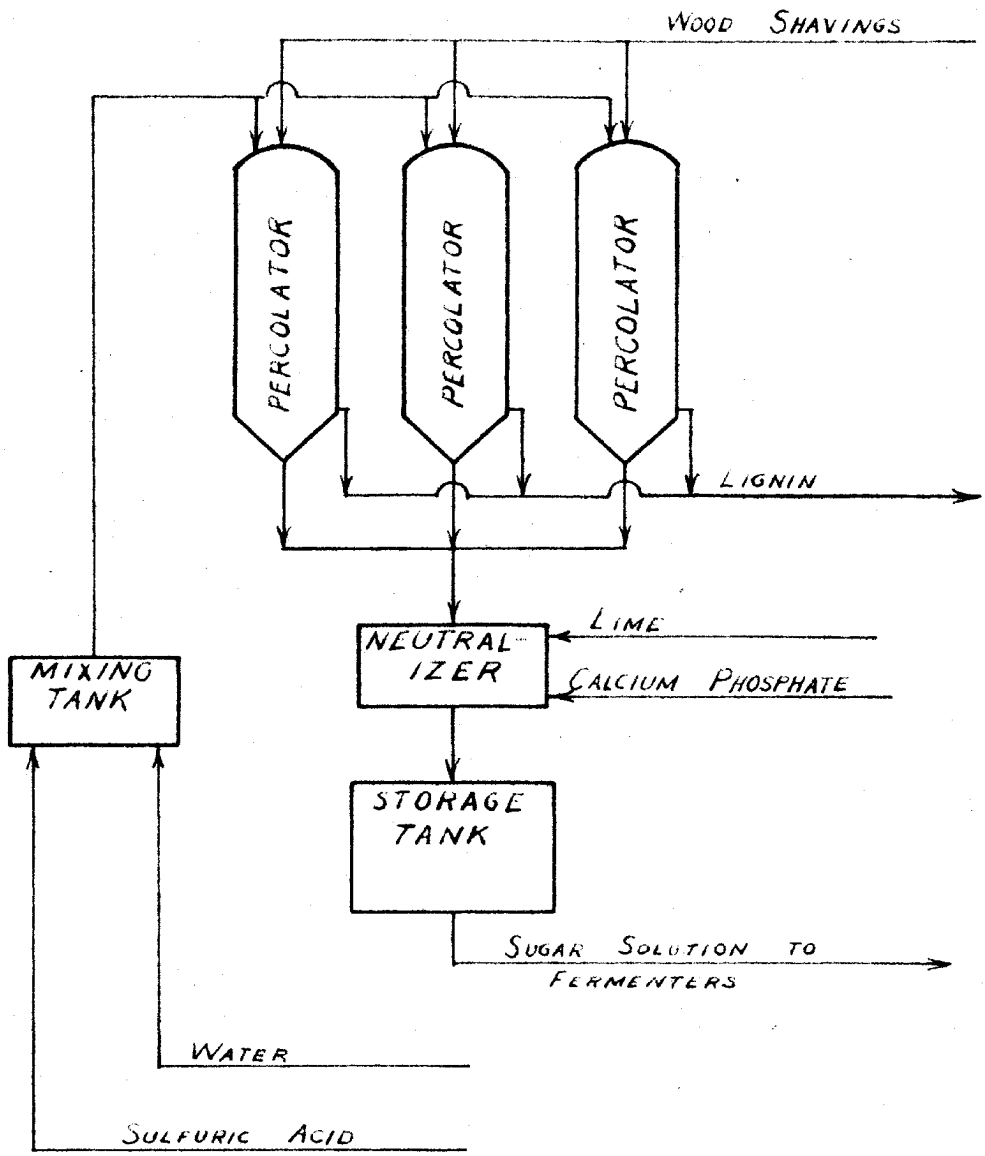


FIG. 3. SCHOLLER-TORNESCH PROCESS FOR SACCHARIFICATION OF WOOD

produce furfural results in a material much higher in the other two principal components, the cellulose and the lignin. In many types of products, such as in the plastics field where a pure source of lignin is not necessary, this raw material would serve admirably. Actually, the cellulose present would be an aid, since it could serve as a filler and strength giving agent. The furfural residue is usually burned under boilers to produce by-product steam.

Furfural may be obtained commercially from oat hulls or other high pentosan containing materials. Dilute sulfuric acid and steam cause the hydrolysis of the pentosans to produce furfural. The steam pressure may vary from below atmospheric to as high as 100 pounds per square inch. The digester used, of course, must be provided with a suitable acid resistant lining. The furfural formed is then passed to a rectification column for concentration. The residue remaining in the digester must be neutralized first if it is to be used as a fuel to produce by-product steam. For this reason lime is added. Following the neutralization the residue is dried and then burned under steam boilers.

To reduce drying costs it is customary not to use a large amount of acid. This sacrifices some of the furfural that could be obtained, but the saving in drying costs counterbalances the value of the additional furfural. As a result a slight amount of the pentosan materials remains.

e. Special methods of lignin isolation. The methods mentioned in the preceding section for the separation of lignin are those of commercial importance, but there are many others than can be used. Some are believed to be much less drastic than the commercially used processes, thus giving a lignin not so degraded nor so changed from the form in

which it exists in the plant substance. In general, lignin isolated by these methods is used largely for research purposes, i.e., problems involving the structure or reactions of lignin.

The methods of separation of lignin fall into the usual two classes. The first removes all other material leaving the lignin behind, while the second involves the solution of the lignin from the cellulose and other accompanying substances.

(1) Removal of other materials leaving insoluble lignin. Lignin may be isolated by the action of sulfuric acid in concentrations varying between 64 and 76 per cent, with 72 per cent being the most common. Lignin obtained in this manner is usually referred to as Klason lignin (89).

Willstätter (157) first proposed using fuming hydrochloric acid in approximately a 43 per cent concentration. This is a very satisfactory method, but it is somewhat more complicated than the sulfuric acid method above.

The use of cuprammonia solution alternated with a boiling of 1 per cent sulfuric acid treatment for hydrolysis of the carbohydrates was proposed by Freudenberg (44).

(2) Solution of the lignin and its subsequent recovery. Several processes have been proposed for pulping which appear to offer promise from an industrial point of view. The three outstanding ones use either chlorine (126)(29), nitric acid (9), or butyl alcohol (8)(10) to dissolve and remove the lignin. The chlorine process is used industrially to some extent, particularly in Italy, France and South Africa. The others have not proceeded beyond the pilot plant stage; however, all may become of importance in the future. In the case of the first, chlorination followed

by treatment with dilute sodium hydroxide renders the lignin soluble and separable from the cellulose and other carbohydrates. A lignin compound containing chlorine is produced. The nitric acid process produces a nitrolignin by the action of dilute nitric acid which is then soluble in dilute sodium hydroxide. The third process, butyl alcohol, dissolves the lignin which may subsequently be recovered by distilling off the alcohol leaving the lignin behind as a solid residue. This latter process gives a lignin more nearly like its condition in the plant substance than any of the other methods.

The isolation of lignin by heating with various materials containing hydroxyl groups in the presence of a catalyst is much used at the present time for obtaining the so-called native lignin. Among the hydroxyl containing materials used are methanol (19), ethanol (63), butyl and amyl alcohols (64), ethylene glycol (73), and the monomethyl ether of ethylene glycol (50). All of these are catalyzed by the addition of small amounts of hydrochloric acid. The lignin may be recovered by dilution with water or by distilling off the volatile solvent. There is evidence to indicate that the hydroxyl containing compounds react chemically with the lignin.

Lignin can also be separated from its associate plant materials by extraction with phenol (88). As with the alcoholic type of solvents, the lignin is heated with phenol and hydrochloric acid. The solution is filtered and then steam-distilled to remove the excess phenol.

Chloracetic acid (111) is reported to remove lignin almost quantitatively from pine wood. It is interesting to note that an organic acid alone is used.

E. Utilization of Lignin

The three principal constituents of plants are cellulose, lignin, and the hemicelluloses. Huge quantities of cellulose are processed industrially and the variety and importance of these uses are tremendous. For the lignin and the hemicelluloses, however, no such widespread usage has developed. As matters have stood in the past, the constituent used has carried the entire cost of production from the source of materials, while the other plant components were either destroyed or thrown away. Utilization of these by-products would aid greatly in decreasing the cost of even the cellulose itself. To serve as a basic raw material, lignin must be available at a cheap price; consequently the basic problem involves finding uses for all three components, thereby decreasing the cost of each individually. Separation must be carried out in such a way as not to destroy the associate materials, as is often the case at present.

Lignin and the hemicelluloses are one of the few remaining examples in industry where such large quantities of waste materials or by-products are thrown away or destroyed. Despite the fact that many of the recent investigations on the utilization of lignin appear encouraging, they still fall far short of using more than a minute amount of the vast quantity produced. As a consequence much remains to be done in this connection.

The most important uses of lignin will be discussed under the particular type of lignin from which they have been derived.

1. Sulfite liquors and basic calcium lignosulfonate

Efforts at the utilization of waste sulfite liquors in the past have

been directed largely toward getting rid of the liquors rather than in developing new uses. Probably the most important reason was the fact that no cheap or easy method was available for the separation of the lignin material. The concentration of sulfite liquors by evaporation is difficult, due largely to their acid nature, high dilution and marked tendency to foam, but the recently developed method of Howard (6), in which the lignosulfonates are precipitated by addition of lime as the basic calcium lignosulfonate, is proving very valuable in the isolation of lignin from the waste liquors.

A promising use of lignin from this source is in the production of vanillin. The basic calcium lignosulfonate is heated with alkali under pressure. The vanillin may be extracted from the mass directly with butyl alcohol (131) or first acidified and then extracted with an organic solvent such as benzene (130). The high quality of lignin vanillin has been fully established and a large portion of the vanillin produced in this country is now made from lignin. In addition, some lignin vanillin is made by processing the whole waste sulfite liquor rather than the precipitated lignosulfonate (74). By-products of this process are various phenols, e.g., guaiacol.

The lignin residue remaining following the alkaline hydrolysis to obtain the vanillin is used in the production of plastics. From it may be prepared a material which is very satisfactory for the production of laminated products. Paper sheets are impregnated with the lignin resin and are then compressed. An excellent field for this type of product is in the manufacture of paper boxes. It is reported that the product has high water and oil resistance (86).

Wallace (148) reports a mixed resinous body made directly from sulfite waste liquor by heating with phenol and formaldehyde. Another method using sulfite waste liquor consists in concentrating and then precipitating the lignosulfonic acid and other organic matter with sulfuric acid. The precipitated material may be molded with or without treatment with phenol and formaldehyde (100).

The colloidal and adhesive properties of waste sulfite liquor lignin have been responsible for its use as a glue, adhesive or cement. Perhaps its most important use along this line is as a binder and dust preventive for secondary roads; it is commonly used for this purpose in Sweden as well as several places in this country (86).

Besides the dissolved lignin, the waste sulfite liquors carry large quantities of carbohydrate substances of which a large percentage is in the form of fermentable sugars which can be used in the production of alcohol and yeast. Practically all the sulfite mills in Germany and many in Scandinavia recover alcohol as a by-product, but none is produced in this manner in the United States (84).

A small amount of lignin from waste sulfite liquors is used in tanning leather as a substitute for tannins (137). A product sold as "Maratan" is made from this source.

It is also reported that the basic calcium lignosulfonate can be used as a Portland cement plasticizer. The plasticity of the fresh concrete is increased, thereby allowing a reduction in the water necessary. The result is increased strength, increased water resistance, and quicker setting (137).

Concentrated solutions of waste sulfite liquor or acidified basic

calcium lignosulfonate solution have a pronounced foaming tendency. It has been reported (93) that evaporated sulfite waste liquor may be used as an ingredient of soap and detergents. As much as 30 per cent can be substituted into laundry soaps with a favorable effect.

Several attempts have been made to produce a good fertilizer from sulfite lignin. Lignin may be ammoniated (123) at high temperatures and pressure. The resulting material has definite fertilizer value, although it is not so satisfactory as commercial fertilizers now in use.

Other suggested uses for basic calcium lignosulfonate are as pigments (83), insecticides and wood preserving agents (85). So far as is known, utilization of lignin in these ways has reached no great importance.

Recently lignosulfonic acids from waste sulfite liquors have been proposed as a raw material for the manufacture of a base-exchange material for water softening (28)(55). Normally the lignosulfonic acids are water soluble, therefore it is necessary to first precipitate and then polymerize the lignin substance with acid in order to make the resulting material water insoluble.

2. Soda lignin

Until quite recently none of the lignin in soda and sulfate liquors was recovered commercially; instead it was disposed of by evaporating and drying, with subsequent burning and final leaching of the residue to recover the soda. The burning process provided the necessary heat requirements for the evaporation and drying step. Today, as pointed out in the section on the isolation of lignin, a product Meadol is now prepared by

precipitation of the lignin in the soda liquors with carbon dioxide, thus allowing its easy recovery.

Most important from the point of view of large consumption uses for lignin is the plastic field. Phillips and Weihe (124) early recognized this in preparing condensation products of acid precipitated soda lignin with aromatic amines and furfural. The products prepared were fusible and readily soluble in organic solvents. A considerable number of patents have been granted on the preparation of lignin molding powders from the waste liquors of this pulping process (138). Addition of phenols and aldehydes and their reaction with the lignin in the alkali liquor previous to precipitation with acid has also been suggested (26). None of these methods, unfortunately, is of significance commercially.

Meadol appears to be finding a definite place for itself in the molding field. It can be used directly as a binder with fibrous materials, forming a hard, dense board on molding. As much as 50 per cent may be incorporated mechanically with phenol-formaldehyde molding powders, thus resulting in a reduction of the binder. Even better results have been secured by substituting Meadol for half of the phenol or cresylic acid in the preparation of thermosetting resins. It has been observed that the resulting molding powder has good flow and cure characteristics, with but slightly decreased strength and increased water absorption (125).

Meadol has been used with success as an expander between the negative plates of storage batteries, where it functions as an efficient depolarizer (125).

Bridger (21), in work conducted in this laboratory, found that acid

precipitated lignin separated by the soda pulping process can serve as an excellent source of many valuable phenolic materials. The lignin was destructively distilled under a vacuum. Higher yields of carbonized residue, tar and methanol are obtained from lignin than from wood. Certain fractions of lignin tar, particularly the phenolic portion, were found to be very satisfactory as a phenol substitute in the phenol-formaldehyde type of plastic. Close fractionation of the lignin tar yielded many valuable phenolic compounds in a pure state. Among those identified, in yields of as high as 5 to 10 per cent based on the tar, were phenol, o-cresol, p-cresol, guaiacol, 3-5 xylenol, and creosol. It was also found that the carbonized residue could be activated to produce a material comparable with many of the commercial activated carbons.

Nelson and co-worker (110) have pointed out that corn stalk soda lignin is very effective as an iron-removal agent for use in water treatment.

As will be pointed out later in this thesis, a very satisfactory base-exchange material for water softening can be prepared from this type of lignin when sulfonated. It compares favorably with many of the commercial type materials of similar nature. Operation as the hydrogen cycle permits the removal of not only calcium and magnesium, but practically all other basic ions present in the raw water.

Although other uses for this type of lignin are mentioned in the literature, little information is available. Some of these are for conditioning boiler water where the lignin produces a softer sludge, for hydrogenation, and for use in paints and ceramics (125).

3. Lignin from the saccharification of wood

Uses for the lignin obtained as a by-product in the Scholler-Tornesch or the Bergius processes have not been developed to the same extent as the other types of lignin. Normally the lignin is briquetted and used as a fuel to provide the necessary heat requirements of the process.

It is reported (12) that this type of lignin can be molded for building purposes without a binder, such as for floors and wall board. Without condensing agents or plasticizers, however, lignin molds to give a brittle product of low mechanical strength.

4. Furfural oat hull residue

Large quantities of high pentosan containing oat hulls are treated with steam and sulfuric acid to produce furfural. The oat hull residue consisting principally of lignin and degraded cellulose serves no use at the present time other than being burned to produce by-product steam, thus aiding in meeting the power and heat requirements of the process.

A possible use of this material is in the plastic field. As will be pointed out later in this thesis, the oat hull residue offers some promise as a raw material for the production of vanillin and syringaldehyde.

5. Lignin in general

Lignin looms as a definite source of many aromatic compounds. To date, although the vast majority of the proposed schemes for utilization have still not passed the laboratory stage, several appear very promising.

Caustic fusion of lignin yields as much as 25 per cent protocatechuic acid, which may then be decarboxylated to give catechol. Catechol is a valuable dihydroxybenzene much used photography.

Hydrogenation of the various types of lignin to give derivatives of propylcyclohexane appears to be another profitable use for lignin. The methyl alcohol, propylcyclohexane and propylcyclohexanol derivatives are valuable solvents. In addition to these, a high boiling resin is produced which may be of use in the paint and varnish industry. Altogether some 90 per cent of the products obtained may be classified in the above three types of substances (66).

III. ORGANIC IONIC EXCHANGE SUBSTANCES

Ionic exchange materials are usually classified in conformity with the type of ion that may be exchanged. Accordingly, the two classes are designated as cationic and anionic exchange materials. Cationic exchange substances are capable of exchanging their positive ions for other positive ions to be found in aqueous solution with which the exchange substance comes in contact. Anionic exchange substances function in a somewhat similar manner, but appear to differ in that entire acid molecules are removed from the aqueous solution rather than anions alone (30).

Cationic and anionic exchange materials may be either organic or inorganic in composition and may be of either natural or synthetic origin. A typical example of an inorganic base-exchange material of natural origin is greensand or glauconite, while the synthetic gel zeolites best typify substances of synthetic inorganic origin.

The phenomenon of base-exchange was first observed with inorganic materials. Way (152)(153), in 1850, is generally credited with having been the earliest to recognize that certain alumino-silicates possessed base-exchange properties. It is reported (102) that in 1858 Eichorn noted that certain natural minerals, chabosite and natrolite, which are complex silicates, had the same properties as the double silicates prepared by Way. In addition, he found that the process could be reversed, i.e., that base-exchange took place. Because the natural minerals tended to swell or boil up when heated with a blow pipe, they were called zeolites, from the Greek words meaning "boiling stone." Gans (58), however, usually receives

credit for having been the first to suggest their application to water softening. Developments in the inorganic zeolite field have been very extensive in the past 20 years and tremendous quantities of water high in dissolved calcium and magnesium salts are now softened by use of this type of exchange material.

For the most part, inorganic exchange materials, particularly the synthetic gel types, are somewhat sensitive to the action of aggressive waters; that is, waters which are very low in silica, or which have a pH of less than 6.8, or which contain less than 10 grains per gallon of hardness (140). Under these conditions the inorganic zeolites show a marked decrease in exchange capacity and some tendency to disintegrate. The organic cation exchange materials, however, are admirably fitted for operation under these conditions. Since they are organic and non-siliceous in composition, silica cannot be extracted. Regeneration may be carried out with either acid or sodium chloride solution, thereby showing their stability to waters of low pH.

The organic cationic exchange materials and the even more recently developed anionic exchange substances have opened up entirely new fields of use in water treatment. No longer is the exchange process limited to the softening of water alone, i.e., to the replacement of the calcium, magnesium, and other cations originally present with sodium ions. Instead, a water may be stripped of all its basic ions, even those of sodium and potassium, when the exchange material is operated on the hydrogen cycle.

The use of cationic and anionic exchange materials in series, the so-called dual ionic exchange process, results in a water of near "distilled

water" composition, since almost all the cations and anions originally present may be removed.

The cost of producing distilled water is an item of considerable expense. In some cases, where large quantities of distilled water are required, the dual ionic exchange process offers definite advantages in providing a water of very low dissolved solids content, since the cost involved in this process is approximately proportional to the total dissolved solids in the water to be treated. For raw waters of fairly low dissolved solids it is more economical to use the dual ionic exchange system rather than to resort to distillation, but when the concentration of dissolved solids in the raw water exceeds a certain value the above is no longer true and it becomes more economical to actually distill the raw water.

The possible uses to which the organic ion-exchange materials may be put are very numerous. Not only may they serve for the softening of water for industrial and domestic use, but there is also a considerable demand for water with a very low solids content for such uses as: high pressure steam generation, beverage manufacture, ice manufacture, textile processing, dye application, drug and chemical manufacture. Added to these may be their use for recovering valuable metallic cations present in very dilute aqueous solutions, such as industrial effluents or mine wastes.

A. Cationic Exchange Materials

The knowledge that organic materials may exhibit base-exchange or ion-exchange is a comparatively recent discovery. It was not until 1927

that Fischer and Fuchs (39) suggested that water could be softened by sodium humates from brown coal. Although they were the first to actually suggest the use of organic materials for softening water, several workers (135)(77), engaged in a study of the role of humus substances on soil acidity, had previously noted that humic substances could undergo ion-exchange. The investigations of these latter workers, however, led them no further than to the function of the humic materials in the soil. Later, in 1931, Borrowman (16) was granted a patent for a process of softening water by passage of hard water through a bed of granular lignite or brown coal. By reason of Borrowman's having put the process into actual practice, Bird (14) credits Borrowman with having been the first to employ organic cationic exchange bodies in water treatment.

The introduction of the sulfonated organic substances and the polyhydric phenol-formaldehyde resins followed at a somewhat later date, both having been introduced within less than a year of each other (112)(107).

From the point of view of cost, the resinous materials are more expensive (38) than either the humates or the sulfonated types. Because of the color throwing defect of the humates, this particular type is gradually being displaced from the market. As a consequence, the sulfonated types furnish the principal competition to the resinous exchangers. The former offers the advantage of lower cost, as well as equal or, in some cases, even slightly higher exchange capacities (107)(102).

1. Humates

Humic substances are widely distributed in nature. The so-called humic acids are the principal components of soil humus and make up some

80 per cent of the organic substances to be found in the soil. They are also found associated with many of the younger types of coal, such as peat and lignite.

Although of indefinite composition, humic acids are characterized by a large number of hydroxyl and carboxyl groups (135). As is the case with lignin, the presence of the aromatic nuclei within the humic acid molecule is well established (54)(40). It is widely believed that lignin is the parent material of humic acid and that the humic acid is merely an oxidized form, the oxidation being brought about by action of certain enzymes and molds present in the soil. Carbohydrate materials can be converted to humin-like materials, although the materials produced are different from natural humic acid, thus tending to substantiate the viewpoint that humic acid is derived from lignin (49).

Shortly before Fischer and Fuchs (39) had suggested that the humates in brown coal underwent base-exchange and that water could be softened by the sodium humates present. Hissink (77), in 1926, had noticed, in his studies on the role played by humic substances in the acidity of various soils, that base-exchange could take place between lime and acid and that the humic substances exhibited greater base-exchange than did the clay associated with the humus in the soil. Burgess and McGeorge (24) have reported on the natural inorganic zeolites present in the soil and the fact that they function in a similar manner. At the time of their discovery, in 1927, Fischer and Fuchs (39) had been primarily interested in studying the ash content of brown coal and thus carried their work no further in the use of the brown coal humates in water softening.

As a consequence, Borrowman (16), in 1931, is generally credited with

having been the first to actually employ organic materials for softening water. His process consisted in passage of hard water through a bed of granular lignite or brown coal, which was regenerated with salt upon exhaustion.

The humate ion-exchange materials possess two distinct disadvantages which have seriously impaired their continued use in softening water, at least since the development of the sulfonated and the resinous types of exchange substances. Their exchange capacity is rather low and, secondly, they tend to throw color, i.e., impart a yellow to brown tint to water after passage through the humate exchange material (25).

In an effort to increase the exchange capacity several methods of treatment have been suggested. Liebkneck (101) states that treatment with water under pressure at elevated temperatures is successful in bringing about this effect. Another investigator (112) proposes the use of such drastic reagents as zinc chloride and phosphoric acid to cause increased exchange capacity of humic acid containing materials.

Various attempts at overcoming the color throwing defect have been proposed. In a later patent Borrowman (17) states that the color throwing defect may be largely eliminated by treatment of humic substances with sodium aluminate. Another patent, assigned to the United Water Softeners of England (146), states that treatment of the exchange material with a solution of a chromic salt is effective in overcoming this latter defect. A patent of similar nature has been granted to Tiger (142) in this country.

The present trend in the organic type of cation-exchange materials appears to be away from the humate type substances in favor of or toward the sulfonated or resinous types. Not only are the color throwing

characteristics of the latter two more satisfactory, but their exchange capacities are considerably higher.

2. Sulfonated substances

It was not until 1935 that the first of the sulfonated types of ion-exchange materials appeared (112). Shortly thereafter a large number of patents were granted abroad for ion-exchange materials of this type. In general, granular organic materials, such as coal, anthracite, coke, peat, lignite, wood, and phenolic resins are treated with sulfonating agents, such as sulfuric acid, oleum, chlorosulfonic acid, sulfur trioxide and various sulfites. It will be noticed that the organic starting materials are substances of high molecular weight that are relatively insoluble in water. Sulfonation of these inserts the sulfonic acid group with its active or exchangeable hydrogen.

The sulfonation treatment must take place at a high enough temperature and under vigorous enough sulfonating conditions to bring about the desired results. On the other hand, too drastic a treatment chars the product and results in a material with only mediocre exchange capacity. One worker (113) proposes passing gaseous sulfur trioxide at a temperature less than 250° C. over anthracite to produce a carbonaceous zeolite. Another (145) states that ion-exchange materials may be prepared by sulfonating peat, lignite, and anthracite with strong sulfuric acid, the reaction being stopped before there is any appreciable amount of charring. Yet another (56) points out that granular coal when treated with a sulfonating agent, e.g., sulfuric acid, oleum, or chlorosulfonic acid, at about 95° C., yields a base-exchange

material. The use of sulfur trioxide dissolved in liquid sulfur dioxide also has been described as an effective sulfonating agent (57).

Zeo Karb, a commercially important ion-exchange material used in this country, is a black granular material which may be prepared by sulfonation with such reagents as fuming sulfuric, sulfur trioxide, or chlorosulfonic acid of carbonaceous materials, e.g., coal, lignite, anthracite, or wood. It is believed that anthracite is the carbonaceous material preferred. Low temperature carbonization previous to sulfonation provides a much more porous structure, thus tending to aid in giving a higher exchange capacity (141).

Burrell (25) reports the preparation of a sulfonated type of exchange material by the treatment of various tannin extractives with sulfuric acid. A number of reactions apparently occur simultaneously. Dehydration, oxidation, sulfonation, and polymerization all play a part in rendering the tannins insoluble and base-exchange active. Included among the materials tested was a hemlock waste sulfite liquor lignosulfonic acid material that had been recovered by evaporation. When sulfonated, this material showed fair exchange capacity, however, it was not so satisfactory as a sulfonated quebracho extract.

In 1938 British (28) and French (55) patents were issued to Crosfield and Sons for the production of a base-exchange material from lignosulfonic acid. Their claim stated that the lignosulfonic acids present in sulfite waste liquors are precipitated by treatment with a strong non-oxidizing acid. The precipitated lignosulfonic acid is then polymerized by the action of more acid and heat to produce an insoluble material. The acid may be

sulfuric. The indurated material may then be sulfonated either before or after granulation.

The above are the only references to be found concerning the use of lignin or lignin materials in the production of ion-exchanging materials. In no case has an effort been made to produce an ionic exchange material from any of the other sources of lignin, such as soda lignin (125) or Klason lignin (89).

3. Polyhydric phenol-formaldehyde resinous materials

The discovery by Adams and Holmes (1) in 1935 that phenol-formaldehyde resins exhibited ion-exchange properties brought forth an entirely new class of materials for use in water treatment. Their development marked the introduction of truly synthetic organic ion-exchange materials. In the case of this type of exchange substance large molecules are built up from small units with the requisite functional groups to provide exchange properties. In the case of the humate or sulfonated types, naturally occurring organic substances of already high molecular weight are either treated or used as such.

Polyhydric phenols are condensed with formaldehyde to yield a resinous type of exchange material. The polyhydric phenolic nucleus of naturally occurring tannins offers a cheap source of raw materials as Holmes (107) early recognized. Burrell (25) showed that tannins of the catechol type produce resins that undergo base-exchange to a high degree. Resins made from monohydric phenols show only mediocre exchange properties (5).

Among the polyhydric phenols or materials containing the same that are condensed with formaldehyde are tannins from various sources (4)(2)

and certain phenolsulfonic acids (37). As stated above, Burrell (25) pointed out that the catechol type tannins, found in quebracho tannin, produce resins with much higher capacities than do tannins from other sources, e.g., logwood extract, hematin, fustic, chestnut extract, tannic acid, gallic acid, and sumac. Most of these latter materials are of the pyrogallol type, rather than the catechol type as is the case with quebracho tannin.

The exchange resin may be considered an insoluble structure of the Bakelite or C-stage type of resin. If the resin is to be operated at a low pH, increased capacity is obtained by the incorporation of strongly acidic groups into the resin "lattice," such as alkyl or aryl sulfonic acids (107). This may be brought about by the condensation of the phenolic material with formaldehyde and sodium sulfite (150), in which case methylene sulfonic acid groups are introduced, or by a condensation of sulfonic acids of aromatic hydroxy compounds (35)(151).

The resinous type of exchange materials offer great possibilities for future development. The nature of their manufacture permits the preparation of individual substances to fill a particular application. At the present time, the Resinous Products and Chemical Company of Philadelphia produces two types of cation-exchange materials, Amberlite IR-1 and Amberlite IR-2. The latter has been highly condensed to give a very hard resistant material which "throws" very little if any color to the treated liquid. The former, IR-1, has a much higher exchange capacity. In principle it is possible to prepare an entire scale of resinous exchangers with practically any desired physical and chemical properties (107).

4. Theory of exchange process

The exact mechanism of the ion-exchange process taking place with the carbonaceous zeolites is not definitely known, but it is fairly well established that the presence of certain functional groups is necessary in order to endow this type of material with ion-exchange properties. These functional groups are all acidic in nature and, accordingly, have an active or replaceable hydrogen which is capable of exchanging with other cations in aqueous solution. The hydrogen may be replaced by the sodium ion and this in turn may be replaced with other ions, such as the divalent calcium and magnesium ions as is the case in water softening. When the cations have reacted with the functional groups of the exchange material they are apparently held in an insoluble form until released by the mass action of the regenerating solution.

As has been pointed out in the preceding section, three classes of cationic exchange materials are used, namely, the humates, the sulfonated substances and the resinous types. In the case of the humates the functional group is a carboxyl group attached to a molecule of such size and such a nature that the compound is insoluble in water (16). With the sulfonated substances the functional group is the sulfonic acid group and, as with the humates, it is fixed to a molecule of sufficiently high molecular weight to be water insoluble. There is evidence to indicate that the sulfonation treatment not only has affixed sulfonic acid groups, but also may have produced additional carboxyl and hydroxyl groups due to the oxidizing action of sulfuric acid at elevated temperatures (25). With the polyhydric phenol-formaldehyde resins, it is believed that large molecules

are built up in a manner similar to that of the phenol-formaldehyde resins, i.e., an insoluble structure of the Bakelite or C-stage type of resin. With the latter class of exchange materials the functional groups are phenolic (107). If the large part of the molecules to which the various functional groups are attached is designated by the letter R, then the formula of the insoluble ion-exchange material is represented by RCOO.H for the humates, $RSO_2O.H$ for the sulfonated substances, and RO.H for the polyhydric phenol-formaldehyde resins. The usual practice, however, is to designate the entire molecule including all of the functional group except the active hydrogen as R. Thus the exchange material may be represented as R.H.

The following reactions illustrate the ionic exchange taking place when various cations are removed from aqueous solution with an acid regenerated carbonaceous zeolite. It is to be understood, of course, that the exchange material may be operated on the sodium cycle as well as the hydrogen cycle and that other cations, e.g., magnesium, iron, or sodium may be removed, in addition to the calcium ion as shown in the equations below.

$$2\ R.H + Ca(HCO_3)_2 = R_2.Ca + 2\ H_2CO_3$$

$$2\ R.H + CaSO_4 = R_2.Ca + H_2SO_4$$

$$2\ R.H + CaCl_2 = R_2.Ca + 2\ HCl$$

To regenerate:

$$R_2.Ca + H_2SO_4 = 2\ R.H + CaSO_4$$

$$R_2.Ca + 2\ NaCl = 2\ R.Na + CaCl_2$$

5. Properties

The cationic exchange materials marketed vary considerably in exchange capacities and in physical characteristics. Some are exceedingly stable and stand up well in service, while others are of rather poor quality.

a. Exchange capacity and physical properties. The exchange capacities of the carbonaceous zeolites extend over a wide range, varying considerably because of such factors as the particle size, the amount of salt or acid used in regeneration and, of course, the class or type of exchange material. The sulfonated materials and the resinous bodies have higher exchange capacities than the humates. In general, both the sulfonated and resinous classes of organic exchangers have capacities equal to and, in certain cases, superior to the best of the synthetic gel types of inorganic cation exchangers.

Table 2, which appears on the next page, provides information concerning the capacities of certain of the various types of cation exchange materials as reported in the literature. Common practice expresses the exchange capacity of ion exchangers in grains of calcium carbonate or equivalent removed per cubic foot of exchange substance. Normally, from 0.35 to 0.5 pound of regenerant is consumed per 1000 grains of exchangeable ion (calcium carbonate equivalent) removed. This corresponds to chemical efficiencies of between 35 to 75 per cent (102).

A wide variation in exchange capacity may be obtained for the same exchange material by use of varying quantities of regenerating solution. In general, however, the use of excessively large amounts of regenerant

Table 2

Exchange Capacities of Various Cation-Exchange Materials

Type of Exchange Material	Capacity in Grains per Cubic Foot	Source
Natural inorganic	2800 - 5500	(102)
Glauconite	2700 - 5500	(118)
Greensand	2600 - 3000	(107)
Synthetic inorganic zeolites	10000 - 13000	(102)
" " "	6000 - 12000	(118)
" " "	4000 - 5500	(107)
Fused zeolites	6000	(118)
Processed clays	5000 - 8000	(118)
Organic exchangers	3000 - 10000	(102)
" "	5000 - 12000	(118)
Zeo-Karb Na^+	11000 - 13000	(129)
Zeo-Karb H^+	15000	(129)
Nalcite "AX" as sodium exchanger	4800 - 7200	(109)
Nalcite "AX" as hydrogen exchanger	2000 - 4000	(109)

is not economical. Two commercial cation exchange materials treated with varying quantities of regenerant show this property as is seen in Table 3. Practically all base-exchange materials show an increase in exchange capacity to a greater or lesser extent when treated with increased amounts of regenerating solution.

In determining the capacities of exchange materials it is customary to use certain definite rates of flow in order to place results on a comparable basis. In Table 2 and Table 3, the samples were operated at a flow rate of 5 gallons per minute per square foot with raw water at a temperature of 70° F. Regenerating solutions of approximately 4 per cent for salt and 2 per cent for acids are common practice.

Table 3

Variation of Exchange Capacity with Quantity of Regenerant Used

Exchange Material	Pounds of Salt per Cubic Foot	Capacity in Grains per Cubic Foot as Calcium Carbonate
Nalcite "AX" (109)	1.5	4800
	2.5	6300
	4.0	7200
Amberlite IR-1 (107)	3.5	8400
	4.0	10000
	5.5	12200
	8.2	14400
	10.5	15500
	11.55	16500
	14.4	18000

When treating waters having a hardness in excess of 10 grains per gallon, and/or sodium salts in excess of 10 grains per gallon, the compensated hardness is used as a basis for calculating the number of gallons of water softened per cubic foot of exchange material. The compensated hardness is the sum of the actual hardness, plus the hardness compensation, plus the sodium salts compensation (109). Table 4 provides the necessary values for obtaining the compensated hardness. The compensated hardness of a water containing 15 grains per gallon of actual hardness and 30 grains per gallon of sodium salts, expressed as calcium carbonate, would be 15 + 1.8 + 1.5 which is equal to 18.3 grains per gallon.

Table 4

Compensation for Hardness and for Sodium Salts (109)

Compensation for Hardness Only		Compensation for Sodium Salts	
Grains per Gallon Actual Hardness	Grains per Gallon Hardness Compensation	Grains per Gallon Sodium Salts as Calcium Carbonate	Grains per Gallon Sodium Salts Compensation
10.0	0.8	10.0	0.6
15.0	1.8	15.0	0.9
20.0	3.2	30.0	1.5
25.0	5.0	45.0	1.9
30.0	6.7		

The average particle size of the organic exchange materials is somewhat less than for greensand and considerably less than for the gel type zeolites. With the sulfonated and the humate classes of organic exchange substances the exchange capacity is markedly affected by the particle size, i.e., the smaller the particle size the higher the exchange capacity. It is reported (107) that with the resinous type of exchange materials, such as Amberlite IR-1, particle size has very little effect on the exchange capacity. This is rather unusual, since with practically all the other carbonaceous zeolites the exchange capacity is very dependent on the particle size or the developed surface.

The organic exchange substances are usually graded to pass a 16 mesh to the inch sieve and to be retained on a 50 to 60 mesh to the inch screen. If the average particle size is very small, considerable pressure drop is encountered when downflow is used, while in the case of upflow a considerable free board space is necessary to prevent the exchange material being carried away. Table 5 shows a typical sieve analysis of Nalcite "AX" and Amberlite IR-1.

Table 5

Sieve Analysis of Nalcite "AX" and Amberlite IR-1

	Nalcite "AX" (109)		Amberlite IR-1 (107)	
Standard Tyler Screen Mesh	Per Cent Retained	Per Cent Cumulative	Per Cent Retained	Per Cent Cumulative
- 16 + 20	32.0	32.0	31.3	31.3
- 20 + 30	40.3	72.3	34.0	65.3
- 30 + 40	19.0	91.3	21.0	86.3
- 40 + 50	5.1	96.4	9.7	96.0
- 50	3.5	100.0	4.0	100.0

The organic cationic exchange substances are characterized by lower densities than the inorganic zeolites, as would be expected. This is somewhat of a disadvantage when upflow conditions are maintained. Table 6 provides information concerning the densities of several of the base-exchange materials available on the market.

Table 6

Apparent Densities of Various Base-Exchange Materials

Material	Density in Air Pounds per Cubic Foot	Source
Greensand	94	(107)
Synthetic Gel Zeolites	55	(118)
Carbonaceous Exchangers	44-49	(107)
Amberlite IR-1	51	(107)
Nalcite "AX"	47	(109)

All of the organic cationic exchange materials imbibe water and swell when the dry product is placed in water. In particular, the resinous exchangers possess this property. Thus, for convenience the Amberlite resins, which swell to a considerable extent when wetted, are furnished in a damp condition in commercial production (107).

b. Equipment requirements and operating details. When organic zeolites are operated on the sodium cycle, equipment may be constructed of materials suitable for use with the inorganic zeolites. Operation on the hydrogen cycle, however, requires that all equipment be of an acid resisting type. As a consequence, it is recommended (109) that ordinary steel be lined with rubber or some acid resistant coating. Wood or stainless steel may be used in an unlined condition. A supporting bed of pure

quartz with a minimum thickness of 12 inches is believed advisable, while the exchange material itself should have a minimum bed thickness of at least 30 inches.

Softeners should be designed for a flow of not more than 5 gallons per minute per square foot of bed area, both when operating and when backwashing. Because of the fairly low density of the carbonaceous zeolites, it is recommended that a freeboard of from 45 - 50 per cent of the bed depth be allowed for backwashing unless a retention screen is provided (109).

Regeneration is carried out by means of either hydrochloric or sulfuric acid in 2 per cent concentration on the hydrogen cycle. In the case of the sodium cycle a five per cent brine solution is preferred. A period of contact of about 30 minutes with the regenerant is advisable. Rinsing at the rate of from 1.5 to 2.0 gallons per minute per square foot of bed area is recommended and should be continued until the effluent is practically free of the regenerating solution (109).

B. Anionic Exchange Materials

The better known anion-exchange materials are resins made by the condensation of certain amines with formaldehyde. As is the case with the cation-exchange materials, both organic and inorganic materials may exhibit anion-exchange and, likewise, both natural and synthetic materials may be used. So far as is known, the anionic exchange materials have not been used industrially except in conjunction with one of the acid regenerated cation exchangers, i.e., when operated as part of the dual ionic exchange

process. The purpose there, of course, is to remove the mineral acids discharge by the cation-exchange substance. Regeneration of the anionic exchangers is brought about by the action of dilute alkali, usually either sodium hydroxide or sodium carbonate.

1. Non-resinous anion-exchange materials

Among the inorganic materials, various insoluble double salts containing aluminum have been proposed for the removal of acids from water or other fluids. Certain iron oxide and aluminum oxide gels (59) are reported to be effective.

Some natural organic materials may be used as such, or may be treated in such a manner as to cause anion or acid exchange. Coal may be chlorinated and then treated with steam (147) to produce an acid adsorber. It is reported that activated carbon (104) has been similarly used. Horn, wool, silk, and leather scrap (116) have also been employed for this purpose. In the latter case, the amine groups of the condensed amino acids making up the protein matter are apparently the functional groups responsible for adsorption of the acid molecules.

At the present time the use of the above materials has not developed to any great extent and the resinous type of exchange materials are by far the more commonly used.

2. Resinous anion-exchange materials

Synthetic resins which exhibited anion-exchange were first prepared by Holmes (3) in 1937 by the condensation of aromatic amines, such as aniline or m-phenylenediamine with formaldehyde. More recently it has

been reported that the condensation of certain amines with aldehydes, such as the monosaccharides (80) also produce a substance having excellent exchange properties. In fact, aniline itself, as well as several other aromatic amines, may be oxidized to insoluble dyes of the aniline black type which are successful in removing acids from water (32)(117). Such materials, however, tend to impart color to the water treated. All of these acid adsorbent materials may be regenerated with dilute alkali.

The condensation of aromatic amines with aldehydes proceeds both on the ring and through the amine groups. The higher the degree of condensation with the amine group, the lower is the acid exchange capacity (22). In order to increase the exchange capacity of the m-phenylenediamine resins, aliphatic polyamines or polyimines are often co-condensed with the resin to give a more basic material (36). Treatment with cyanamide or dicyanamide will introduce the strongly basic guanidino group, thus bringing about this effect.

As in the case of the cationic resinous type of exchange material, it is possible to produce a product to meet a particular type of use. The Resinous Products and Chemical Company of Philadelphia markets two types of anion-exchange materials, Amberlite IR-3 and Amberlite IR-4. The former is highly condensed to give a product which is very hard and which has superior properties in regard to "color throwing," but the latter has a much higher exchange capacity.

The resinous type of anionic exchange materials are characterized by high stability, high exchange capacity, high rate of exchange and very satisfactory color throwing properties. Unfortunately, their price is still rather high.

3. Theory of exchange process

It has been widely believed (15) that the resinous anion-exchange materials exist as organic bases with ionizable hydroxyl groups and that when an acid, such as hydrochloric acid, comes in contact with an anionic exchange substance in the basic state, the chloride ion of the hydrochloric acid displaces the hydroxyl ion which is then free to combine with the hydrogen ion of the acid to form water. Recent work on this phase of the mechanism of anion exchange indicates that the preceding concept is in error and that, instead, the exchanger adsorbs whole molecules of acid and that very little neutral salt cleavage occurs (30); however, easily hydrolyzable salts such as those of aluminum and iron may be split by anion exchangers. Apparently the exchanger adsorbs the acid formed by hydrolysis, thus disturbing the equilibrium and causing the salts to continue to hydrolyze because of the removal of one of the products, the acid in this case.

The probable explanation of the fact that entire acid molecules are adsorbed rather than just anions alone is that the basic amine groups of the resinous exchangers react with acids in the same manner that hydrochloric acid reacts with aniline. In the latter case soluble aniline hydrochloride is formed. With the anion-exchange resins, the amine groups are attached to very large molecules; molecules of sufficiently high molecular weight to render the exchange material insoluble in aqueous solution, even when the resinous amine hydrochloride is formed. Thus the acid is removed from the solution. Regeneration with dilute alkali restores the exchanger back to its original form by neutralization of the acid.

The anionic exchange substances do not adsorb carbonic or other weak acids to any great extent; however, they have excellent capacities for the stronger acids, such as hydrochloric or sulfuric acids (107).

A two per cent sodium carbonate solution or a 0.5 per cent solution of sodium hydroxide is customary for regeneration. Strong caustic solutions tend to cause color throwing or eventual solution and disintegration of the resins.

If the letter X is allowed to represent the anion-exchange resin, then the reaction taking place in acid-adsorption may be represented by the following reaction:

$$X + HCl = X.HCl$$

To regenerate:

$$X.HCl + NaOH = X + NaCl + H_2O$$

$$X.HCl + Na_2CO_3 = X + NaCl + NaHCO_3$$

4. Properties

The anionic exchange materials available on the market are principally of the resinous type. Practically no information is available on other types of acid adsorbents. The aromatic diamine resins prepared by early workers had the disadvantage of a tendency to "leak" anions and, in addition, rather low capacities. However, since that time improved aromatic diamine resins have been synthesized which, to a large extent, have overcome these defects (107).

a. Exchange capacity and physical properties. The resinous types of anionic exchange materials have exhibited a marked dependence of exchange

capacity upon particle size, as distinguished from the resinous type of cationic exchange materials mentioned earlier. Table 7 illustrates the relation between the particle size of Amberlite IR-4 and the exchange capacity. As with the cation-exchange materials, capacities are reported as grains of acid (calcium carbonate equivalent) adsorbed per cubic foot of exchanger.

Table 7

Relation of Acid Adsorption Capacities and Particle Size of an Anionic Exchanger (107)

Standard Tyler Screen Mesh	Capacity in Grains per Cubic Foot
- 12 + 20	1,550
- 20 + 30	6,000
- 30 + 40	13,200
- 40 + 50	20,000
- 50 + 60	23,000

Anion exchangers show a greater exchange capacity for sulfuric acid than for hydrochloric acid, as is shown by Table 8.

Table 8

Adsorption of Hydrochloric and Sulfuric Acid by Amberlite IR-4 (108)

Capacity, as Calcium Carbonate, Expressed in Grains per Cubic Foot	Pounds of Sodium Carbonate per Cubic Foot Used in Regeneration	Pounds of Sodium Carbonate Used in Regeneration per 1000 Grains of Anion Removed
For hydrochloric acid 20,000	10.0	0.50
For sulfuric acid 45,000	22.5	0.50

The particle size distribution of the resinous anion exchangers is quite similar to that of the corresponding resinous cation exchangers. Table 9 gives the wet screen analysis of Amberlite IR-4.

Table 9

Sieve Analysis of Amberlite IR-4 (108)

Standard Tyler Screen Mesh	Per Cent Retained	Per Cent Cumulative
- 16 + 20	0.9	0.9
- 20 + 30	39.5	40.4
- 30 + 40	35.8	76.2
- 40 + 50	16.6	92.8
- 50 + 60	4.5	97.3
- 60	2.7	100.0

The resinous exchangers are usually shipped wet so that no swelling takes place on further wetting. In this condition the density is approximately 36 pounds per cubic foot (108).

The anion-exchange resins exhibit a large amount of swelling during the course of the exchange cycle. Amberlite IR-4 swells as much as 25 to 30 per cent when saturated with acid, although when the bed is regenerated it shrinks to its original volume (108).

b. Equipment requirements and operating details. The equipment used in connection with the anionic exchange materials must be resistant to both alkali and acid. Rubber lined equipment probably meets this demand more satisfactorily than any other material of construction.

It is recommended (108) that a very high freeboard be provided to prevent loss of the resin during backwashing. The swelling property of

this type of resin is largely responsible for the unusually high freeboard of 75 per cent that is suggested unless a retention screen is used.

Downflow operation is recommended and an operating rate of 5 gallons per square foot per minute should not be exceeded. Regeneration should be carried out at a rate between 1.0 to 1.5 gallons per square foot per minute with a sodium carbonate solution of about a two per cent concentration (108). Caustic solutions of as high as 3 per cent are reported to be injurious to anion-exchangers, consequently regenerating solutions of not greater than 0.5 per cent sodium hydroxide are recommended (15). A rinse rate of from 1.5 to 2 gallons per minute is reported to be satisfactory.

IV. EXPERIMENTAL ORGANIC IONIC EXCHANGE SUBSTANCES

While investigating various ways in which lignin might be utilized, it was discovered that an excellent cationic exchange material could be prepared from soda lignin, i.e., lignin recovered from the waste pulping liquors or black liquors of the soda pulping process. As a result of the promise shown by lignin from this source, other types of lignin or high lignin containing materials were also investigated, in particular those of an agricultural by-product nature. Anionic exchange materials were also prepared from lignin.

A. Cationic Exchange Substances

The method used in the preparation of the cationic exchange materials consisted essentially of the sulfonation of lignin. The sulfonation treatment involved not only the direct insertion of sulfonic acid groups into the lignin molecule, but also involved various secondary reactions, such as oxidation, dehydration and polymerization. The extent to which these various secondary reactions take place is determined largely by the conditions employed. In order to secure information regarding the preparation of materials with high exchange capacities and satisfactory physical properties, a study was made of the effect of the principal variables involved, i.e., temperature, sulfonating acid concentration and the ratio of the amount of lignin to acid.

1. Materials used

The basic raw materials were lignin and sulfuric acid. Two concentrations of commercial sulfuric acid were used: ordinary concentrated sulfuric acid of 66 degrees Baume' or 93.2 per cent strength and 20 per cent free sulfur trioxide fuming sulfuric acid. Both were manufactured by the General Chemical Company of New York.

The major portion of the work was done using lignin separated by the soda pulping process. Meadol, a commercial alkali lignin product from the spent liquors of the soda paper pulping process precipitated by carbon dioxide, was obtained from the Meade Paper Company of Chillicothe, Ohio. Cornstalk soda lignin, prepared in this laboratory according to the method suggested by Bridger (21), was also employed. Hydrochloric acid rather than carbon dioxide was used to precipitate the lignin from the spent alkaline cook liquors.

Another distinctly different type of lignin was employed, namely, Klason lignin. This type of lignin was prepared by hydrolysis of the cellulose and other carbohydrate materials with 72 per cent sulfuric acid leaving the lignin behind in an insoluble form. The raw material used for obtaining this type of lignin was the residue from the dilute sulfuric acid and steam treatment of oat hulls to obtain furfural. This is usually known as the furfural oat hull residue. The furfural oat hull residue was obtained from the Quaker Oats Company of Cedar Rapids, Iowa.

2. Preparation of lignin

a. Lignin from cornstalk soda cook liquors. The procedure used was

that proposed by Bridger (21) for the recovery of lignin from cornstalk or corncob cook liquors in which the ratio of the weight of stalks to caustic soda was 10 to 1. After the liquor from the cooker had been strained through a cloth to remove any large particles, it was evaporated in a large kettle until the specific gravity at 90° C. was 1.06. The liquor was then removed from the kettle, weighed and placed in a lead lined acid resistant kettle. For each pound of concentrated liquor 75 milliliters of commercial hydrochloric acid were added slowly with stirring. The acidified liquor was brought to a slow rate of boiling. After two hours of boiling the coagulated lignin was filtered out of the mixture in a stone suction filter. The precipitate was then washed several times with water and was finally dried in air.

b. Klason lignin from furfural oat hull residue. The furfural oat hull residue was stirred into 72 per cent sulfuric acid (84) in which 10 milliliters of the acid solution were present for each gram of the furfural oat hull residue. The mixture was cooled so that the temperature did not rise above 20° C. It was then allowed to stand approximately 16 hours at room temperature. Next water was added until the ratio of acid to water by volume was 1 to 37. After being boiled gently in a lead lined kettle for 4 hours the product was filtered in a stoneware suction filter and was washed several times with hot water. The lignin residue was then oven dried at 100° C.

Based on the dried furfural oat hull residue, a yield of 40 per cent of lignin was obtained. Since the procedure followed is essentially the same as that used quantitatively, only on a larger scale, the results

indicate that the lignin content of the furfural oat hull residue is approximately 40 per cent. Cellulose and a small percentage of undecomposed pentosan materials constitute the remaining 60 per cent.

3. Preparation of samples

The preparation of the cationic exchange materials developed during the course of this investigation involved four distinct steps, namely: (1) sulfonation, (2) washing, (3) drying, and (4) reduction to proper particle size.

a. Sulfonation. Three variables markedly affect the exchange material during this step. They are: (1) temperature, (2) the ratio of the amount of sulfuric acid to lignin and (3) the concentration of the sulfonating acid.

It was early discovered that the temperature must be closely controlled during the sulfonation period. A temperature variation of as little as 10° C. will alter radically the exchange capacity and, to some extent, the physical properties, such as density and structure. Accordingly, a standard method of preparing samples was devised which allowed for close temperature control.

The sulfonation was carried out in a two or three liter beaker. The beaker, containing the sulfuric acid and lignin mixture, was placed in a 2 gallon enameled pail. When sulfonating at temperatures below 90° C. water was used as the heat transfer medium, but at higher temperatures a good grade of colorless mineral oil was used. The oil or water level in the pail was maintained at such a level as to extend several inches above the height of the sulfuric acid and lignin mixture within the beaker, thus functioning as a constant temperature bath. Thermometers were hung from

a ring stand into both the outer bath and the beaker in which sulfonation was being carried out. In this way it was possible to maintain close control of the temperature of the lignin-sulfuric acid mixture. In no case was a variation of more than plus or minus 2° C. allowed from the desired temperature. The sulfonating mixture was hand stirred during the entire period of treatment. The oil or water bath was heated by a small single plate gas stove with two heating units. One heating unit was of small heating capacity and the other was of high capacity, thus making it possible to vary the rate of heating over a wide range. This plus the buffering action of the oil or water bath provided extremely flexible temperature control during the sulfonation process.

In order to have on hand a sufficient amount of exchange material for the various tests conducted, 150 grams of oven dried lignin were sulfonated in each of the tests. The amount of sulfuric acid used was varied over a wide range to determine the effect of this variable on the type of product obtained.

It was found necessary to add the lignin to the cold sulfuric acid slowly with constant stirring, otherwise the powdered lignin tended to become lumpy. When added slowly, the lignin dissolved, or dispersed, into the sulfonating medium. Lignin and sulfuric acid react exothermically, consequently it is necessary to start the addition with cold acid, otherwise the reaction will rapidly get out of hand because of an increasingly large amount of foaming due to sulfur dioxide formation as the temperature rises. With low ratios of sulfuric acid to lignin the heat liberated was sufficient to elevate the temperature of the mixture some 70° C. As a result, the oil of the water bath was usually maintained at a temperature considerably below

the desired sulfonating temperature during the early stages in order to remove heat and thus not allow the temperature to rise above that desired. After the initial exothermic reaction had taken place the oil bath was heated rapidly in order to bring the sulfonating mixture to the desired temperature. When sulfonating at temperatures above 100° C. the action of the sulfuric acid was strongly oxidizing in nature and thus tended to cause a further temperature increase, thereby making it necessary to maintain the temperature of the bath at approximately 5° to 10° C. below that desired for sulfonating in order to remove the additional heat produced because of this effect.

With lignin separated from its associate plant materials by the soda pulping process, e.g., Meadol, it was observed that at low temperatures, below 80° C., very little sulfur dioxide was formed and that the predominant reaction appeared to be sulfonation. The lignin dispersed in the acid with some difficulty and there was a tendency to form lumps. Very little foaming was noted and no great amount of polymerization or gelling took place as with samples prepared at higher temperatures. After some time, however, the mixture tended to become quite viscous. With samples prepared between 80° and 100° C., the tendency to form lumps disappeared and smooth dispersions were formed. In this temperature range, sulfur dioxide evolution became quite pronounced. This, in turn, caused foaming. Rapid stirring and use of a beaker of larger size, 3 liter, aided in the solution of this difficulty. Thus, at higher temperature, it appeared that sulfuric acid was becoming an oxidizing as well as a sulfonating agent. When gelation took place, the lignin-sulfuric acid mixture first became quite viscous, then plastic and finally formed a gel. Usually the gel was black and glistening and fairly

rigid in structure. At temperatures in excess of 100° C. the lignin dispersed very readily in the acid. Large amounts of sulfur dioxide were given off. Within a short time, usually in less than 20 minutes, the mixture would gel to form a very porous, low density mass, resembling in structure a beaten egg white. After a further interval of time the mass became very rigid in structure.

Little difficulty was encountered in dispersing Meadol in the sulfonating mixture when high ratios of acid to lignin were employed. The viscosity of the lignin-sulfuric acid mixture was very much less at these high ratios, as would be expected. In addition, the tendency to foam was very much reduced, apparently largely due to the decreased viscosity of the mixture. The interval of time before gelling took place was considerably longer when high ratios of acid to lignin were used than with low ratios. The gels formed in the case of the former were much softer and not so tough nor so hard as with the latter.

Meadol did not dissolve readily in sulfuric acid concentrations of less than 90 per cent at temperatures below 85° C. When acids more dilute than this strength were used gelling did not occur unless the sulfonation temperature was above 85° C. The higher the concentration of the acid used for sulfonation the shorter was the time before polymerization set in. With 20 per cent fuming sulfuric acid polymerization occurred before all of the lignin could be added. When gels were formed with dilute sulfonating mixtures they did not appear so homogeneous as when concentrated or fuming sulfuric acid was used.

The furfural oat hull residue and the Klason type lignin obtained from this raw material differed somewhat from the soda type of lignin, e.g.,

Meadol, when sulfonated. Solution did not take place during the sulfonation process. Considerable swelling of the insoluble material took place, but even after sulfonation the resulting material appeared to retain the original oat hull structure. Little tendency to foam was noted. Otherwise the behavior was very similar to that of Meadol, particularly so in regard to the effect of temperature.

b. Washing. A large amount of sulfuric acid was held within the gel-like structure of the sulfonated Meadol. It was necessary to remove this acid, otherwise the exchange material did not show ion-exchange properties nor did it harden satisfactorily. In addition, if the acid was not removed further action of the remaining acid took place when the exchange material was dried.

Immediately following the sulfonation step the product was poured into a large evaporating dish and allowed to set for 24 hours. During this time the gel structure developed further.

Water was then poured on the sulfonated lignin mixture in the evaporating dish. As the sulfuric acid was leached out, the gel became much harder forming a hard glistening surface even when fractured or cut. The wash water containing the sulfuric acid leached from the material was poured out of the dish and fresh water was added to continue the leaching operation. After several washings the sulfonated Meadol became quite hard. It was then cut or broken into smaller pieces in order to provide more surface. Seven or eight washings were usually necessary to remove the acid. Upon removal of the acid the resulting material was quite hard and when broken gave a smooth fracture.

Samples prepared at above 85° C. colored the wash water only slightly

after the first two or three washings. The tendency to color the wash water became less pronounced as the temperature of sulfonation was increased. At above 100° C. no tendency to color the water during washing was noted. With sulfonation temperatures below 85° C. a decided brownish color was imparted to the wash water. This was no doubt connected with the fact that polymerization had not taken place to any great extent at low temperatures and the usual gel structure had not developed. In addition, low temperature sulfonated materials showed a tendency to disintegrate to smaller sized particles.

c. Drying. After the exchange materials had been washed free of residual acid they were then dried at 100° C. in a laboratory drying oven. Upon drying the exchange material was observed to shrink considerably in volume and at the same time it became much harder. There was some tendency for the larger particles to break or fracture as drying proceeded, apparently to relieve stresses introduced as shrinking took place.

Drying not only hardens the exchange materials, but also aid in its "stabilization," that is, in decreasing the tendency to impart color later to the water being softened. Samples dried at higher temperatures, e.g., 100° C., were found to have a much less "color throwing" tendency than samples dried at lower temperatures, e.g., 50° C.

d. Reduction to size. The dried exchange materials were reduced to the necessary particle size by crushing in a mortar. Samples were then sieved in Tyler Standard screens. Three samples were screened to the following particle sizes: (1) passing 10 mesh and retained on 20 mesh, (2) passing 20 mesh and retained on 35 mesh, and (3) passing 35 mesh and retained on 48 mesh. This is the approximate range covered by the com-

mercial carbonaceous zeolite materials now on the market. The three screenings were investigated in order to determine the variation in exchange capacity with average particle size.

4. Testing and analysis of samples

The cationic exchange materials prepared were tested for exchange capacity when operated on both the sodium and the hydrogen cycle. In addition, samples were analyzed for sulfur in an effort to determine whether any correlation existed between the exchange capacity and the sulfur content.

The glass columns used in this investigation were of Pyrex glass, with an internal diameter of 21/32 inch and an overall length of 12 inches. The height of the exchange material within the tubes varied between 6 and 10 inches. Glass wool plugs at each end served to hold the exchange substance in place.

All samples were packed wet. Previous to placing in tubes the exchange material was soaked in water in order to allow any swelling to take place. The samples were then poured into the column and allowed to settle freely in water.

Downflow operation was maintained, both when testing samples and when regenerating. A rate of 20 milliliters per minute was used when softening. When regenerating a rate of between 5 to 10 milliliters per minute was used. A rinse of 100 milliliters at a rate of 50 milliliters per minute was employed following regeneration. When regenerating on the sodium cycle 200 milliliters of 4 per cent salt were used and when regenerating on the hydrogen cycle 200 milliliters of 2 per cent, by weight, hydrochloric acid.

The hard water used in testing samples was taken from the mains of the Iowa State College. This water had a uniform hardness or 23.5 grains per gallon. The softened effluent from the exchange materials was tested at least every 200 milliliters discharged until the break-through. In all cases the break-through was very sharp and was evidenced by a sudden increase in the soap titration value above the usual amount of 0.5 milliliters of soap solution per 50 milliliter sample for completely softened water. A 0.06 N potassium oleate solution in 80 per cent ethyl alcohol was used in the soap hardness test. When operating on the hydrogen cycle it was necessary to neutralize the softened acid effluent previous to testing for softness with soap solution. This was done by titration of the acid with 0.1 N sodium hydroxide solution using bromthymol blue as an indicator.

The sulfur content of the exchange materials was analyzed using the well known Eschka method. Samples were mixed with Eschka's mixture, anhydrous magnesia and sodium carbonate, and were then oxidized in an electric muffle at a maximum temperature of approximately 850° C. One hour was used to bring the cold muffle with the samples to the required temperature. Following this the muffle was maintained at 850° C. for 1 and 1/2 hours. The calcined mixture was dissolved in water and oxidized with saturated bromine water so that all the sulfur present was oxidized to the sulfate form. The solution was acidified with hydrochloric acid and the excess bromine boiled off. The sulfate ion was then precipitated with barium chloride as barium sulfate and was weighed as such. The samples analyzed for sulfur were those passing 35 mesh retained on 48 mesh which had been used previously for securing the exchange capacity.

5. Results

The results presented in Tables 10 to 16 show that it is possible to prepare cationic exchange materials from Meadol which are comparable to and, in some cases, are superior to commercial exchange materials now being marketed. By varying the conditions of treatment during the sulfonation step exchange materials may be made which possess a wide range of properties.

In Tables 10, 11, and 12 the results of the investigation of the effect of temperature and varying concentrations of sulfonating acid at a constant ratio of acid to lignin are shown. Increase in temperature of sulfonation caused an increase in exchange capacity on the weight basis. This conclusion is illustrated graphically by Figure 6. In general, for the exchange capacity on the volume basis, a maximum exchange capacity occurred between 85° and 95° C. In particular, this latter observation applies to the coarse screened samples. To illustrate graphically, the volumetric exchange capacity versus temperature for the samples passing 10 mesh retained on 20 mesh of Table 10 have been plotted in Figure 4. Similar results regarding the temperature at which a maximum volumetric exchange capacity occurred were noted for the fine screened samples, but the data obtained were not so consistent nor satisfactory for plotting as for the coarse screened samples with the exception of Figure 5 in which data from Table 13 have been plotted.

The reason for the sudden decrease in capacity on the volume basis as the temperature of sulfonation increased is apparent when it is noted that a sharp decrease in density took place with rise in temperature. A decrease

FIGURE 4

EFFECT OF TEMPERATURE ON VOLUMETRIC EXCHANGE CAPACITY

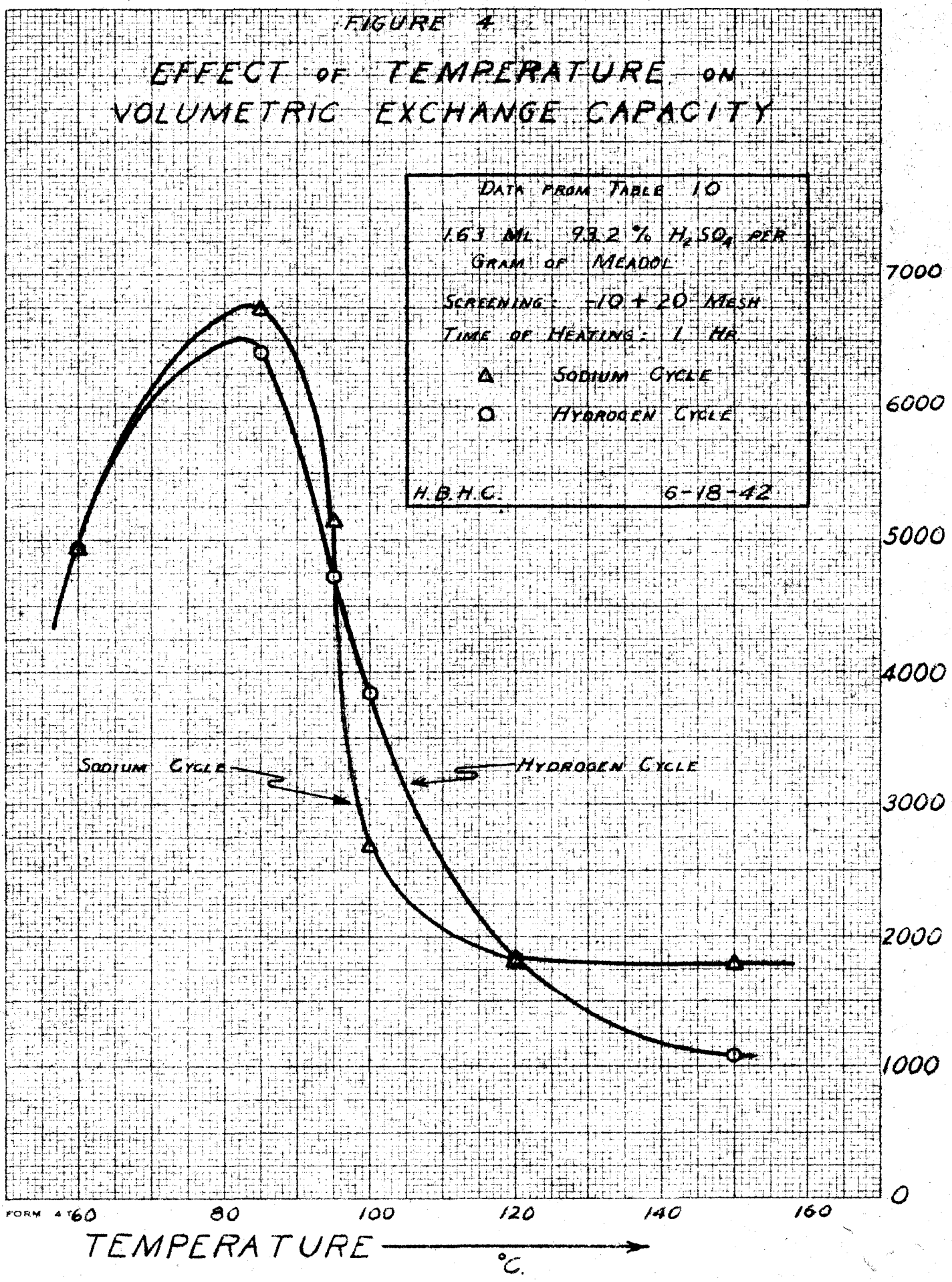


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Table 10

Effect of Temperature with 93.2 Per Cent Sulfuric Acid

Ratio of Sulfuric Acid to Meadol = 1.63 ml. 93.2 Per Cent H_2SO_4 per Gram of Meadol
Time of Heating = 1 hr.

Sample No.	Sulfonation Temperature °C.	Particle Size Mesh	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
1	60	-10+20*	35.2	269	269	4930	4930	
		-20+35*	29.4	280	260	5520	6820	
		-35+48*	38.3	237	267	5960	6710	1.43
2	85	-10+20*	42.0	293	308	6410	6740	
		-20+35*	36.9	271	287	5990	6340	
		-35+48	35.9	294	313	5600	5960	2.30
3	95	-10+20	34.0	218	235	4720	5150	
		-20+35	37.9	279	312	6330	7080	
		-35+48	37.4	374	391	8870	9280	2.15
4	100	-10+20	24.1	295	207	3840	2690	
		-20+35	34.2	275	295	5430	5780	
		-35+48	38.7	335	367	7600	8320	1.94
5	120	-10+20	16.5	251	251	1830	1830	
		-20+35	25.0	377	448	5630	6690	
		-35+48	27.5	448	527	6240	7340	1.65
6	150	-10+20	13.0	142	237	1090	1810	
		-20+35	25.5	387	592	6020	9210	
		-35+48	27.1	438	525	6750	8110	1.12

*Disintegrated during course of testing.

Table 11

Effect of Temperature with 99 Per Cent Sulfuric Acid

Ratio of Sulfuric Acid to Meadol = 1.63 ml. 99 Per Cent H_2SO_4 per Gram of Meadol
Time of Heating = 1 hr.

Sample No.	Sulfonation Temperature °C.	Particle Size Mesh	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
7	60	-10+20*	36.8	331	298	7040	6340	
		-20+35*	37.0	348	315	7200	6520	
		-35+48	37.7	368	310	7180	6050	2.41
8	85	-10+20	39.2	205	264	4800	6160	
		-20+35	39.9	226	282	5630	7040	
		-35+48	39.1	337	323	8340	8010	2.61
9	95	-10+20	31.7	226	303	4340	5790	
		-20+35	34.3	356	356	7400	7400	
		-35+48	36.2	428	409	8820	8440	2.77
10	100	-10+20	34.2	141	123	2850	2500	
		-20+35	35.6	205	280	4480	6090	
		-35+48	38.8	293	351	6340	7600	2.13
11	120	-10+20	12.3	271	380	1620	2270	
		-20+35	28.6	461	512	6700	7450	
		-35+48	27.5	655	634	10210	9860	1.76

*Disintegrated during course of testing.

Table 12

Effect of Temperature with 87.8 Per Cent Sulfuric Acid

Ratio of Sulfuric Acid to Meadol = 1.63 ml. 87.8 Per Cent H_2SO_4 per Gram of Meadol
Time of Heating = 1 hr.

Sample No.	Sulfonation Temperature °C.	Particle Size Mesh	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
12	85	-10+20	----	----	----	----	----	
		-20+35	42.7	259	222	5630	4830	
		-35+48	39.6	233	251	5400	5820	1.67
13	100	-10+20	37.2	172	190	4150	4570	
		-20+35	41.4	181	195	4730	5070	
		-35+48	41.9	183	237	4960	6450	1.57
14	125	-10+20	23.0	162	194	1780	2140	
		-20+35	33.5	231	373	4380	7090	
		-35+48	37.1	222	347	5560	8680	1.37
15	150	-10+20	22.6	262	373	2450	4170	
		-20+35	25.0	420	589	5750	8060	
		-35+48	29.5	342	492	5270	7560	1.20

Table 13

Effect of Temperature with 93.2 Per Cent Sulfuric Acid

Ratio of Sulfuric Acid to Meadol = 2.17 ml. 93.2 Per Cent H_2SO_4 per Gram of Meadol
Time of Heating = 2 hr.

Sample No.	Sulfonation Temperature °C.	Particle Size Mesh	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
16	85	-10+20	42.1	196	196	5200	5200	
		-20+35	43.1	214	249	6080	7090	
		-35+48	45.9	282	296	6940	7290	2.00
17	95	-10+20	39.4	334	351	6940	7290	
		-20+35	38.1	341	341	7020	7020	
		-35+48	42.1	384	401	8200	8570	2.57
18	100	-10+20	38.4	278	297	5070	5390	
		-20+35	38.2	310	326	6410	6770	
		-35+48	39.5	368	368	7770	7770	2.53
19	125	-10+20	26.9	164	273	2000	3330	
		-20+35	27.1	337	359	5060	5400	
		-35+48	27.4	381	476	6670	8330	1.81

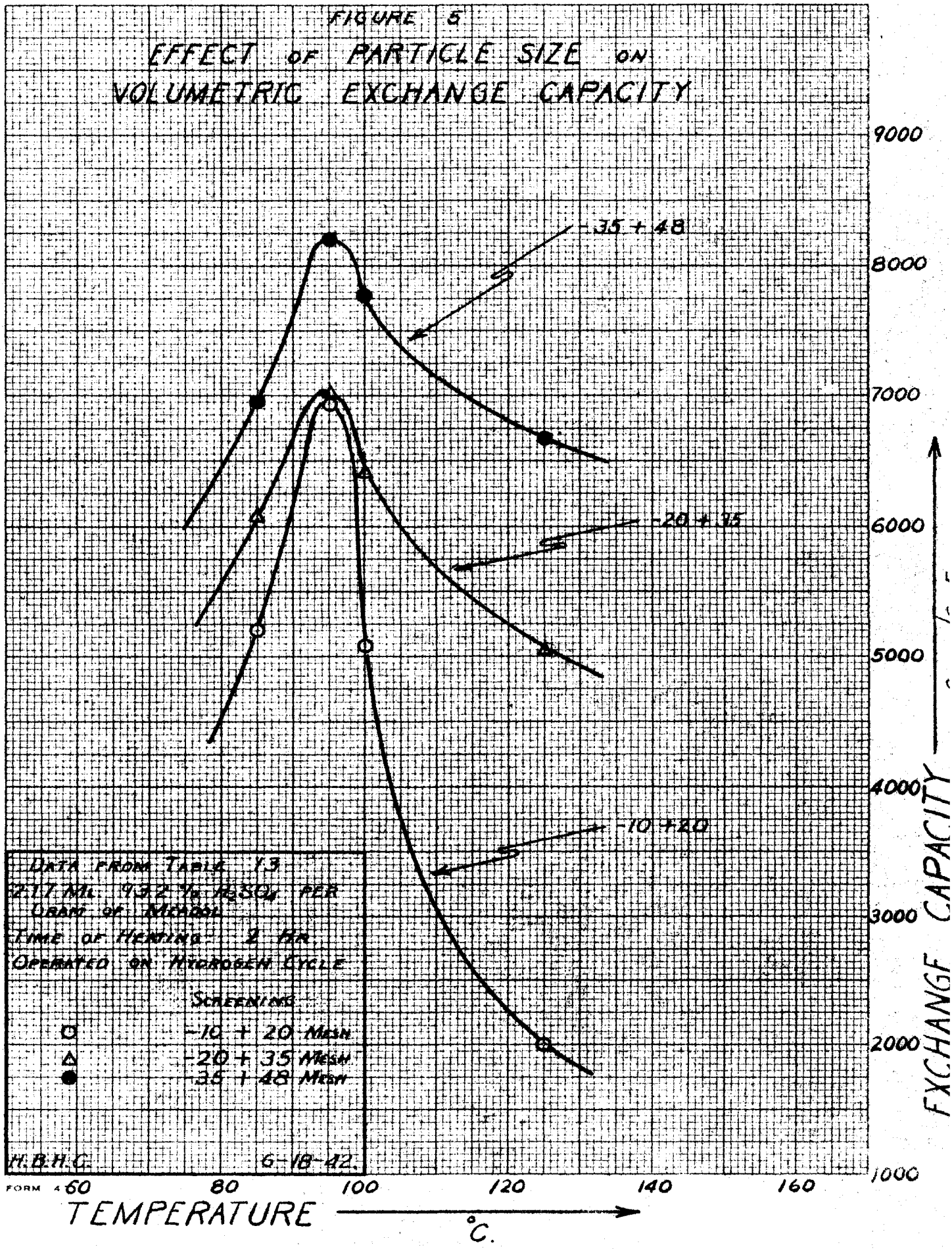
in density means less exchange material is present per cubic foot, thus explaining the decrease in volumetric exchange capacity even though the exchange capacity on the weight basis has increased gradually at the same time. The large decrease in density with increase in temperature for the sulfonated lignin, especially for the coarse screened samples, is apparently due to the fact that sulfur dioxide evolution occurs to the greatest extent during the early stages of sulfonation and, as a consequence, when setting takes place within or during this period a large amount of the gas is trapped. The result is a material that is very porous in structure. For the most part the bubbles trapped were of fairly large size, thereby affecting the larger particle size samples to the greatest extent.

As would be expected, the finer particle size samples showed higher exchange capacities, both on the volumetric and on the weight basis. Figure 5, taken from data in Table 13, shows this effect. Exceptions to this generalization are to be found with Samples 1, 2, and 7. All of these samples were prepared at temperatures of 85° C. and below and, as was mentioned previously, gelling did not occur. Instead, the fine particles cemented together on drying and remained in that condition through the sieving step. While being tested, the cemented particles disintegrated to their original finely divided state, thus giving results not indicative of the large particle size samples which supposedly they represented.

The concentration of the sulfonating acid markedly affects the exchange capacity. A comparison of Tables 10, 11, and 12 illustrates this fact. In Table 10 sulfuric acid of 93.2 per cent concentration was used; while in Table 11 and Table 12 acids of 99 and 87.8 per cent concentration, respectively, were used for sulfonation. In general, the higher the

FIGURE 5

EFFECT OF PARTICLE SIZE ON VOLUMETRIC EXCHANGE CAPACITY



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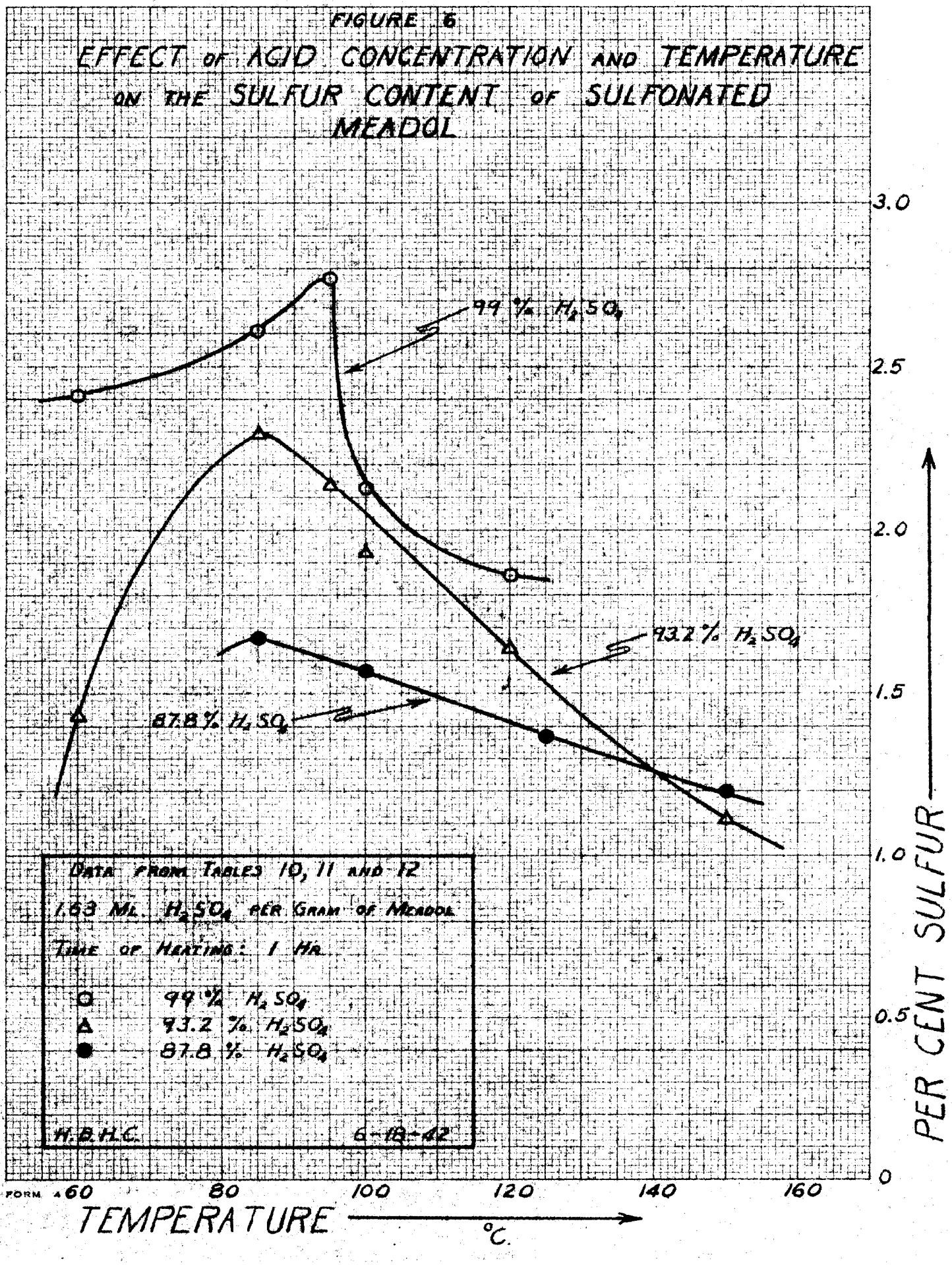
concentration of the sulfonating acid used the higher is the exchange capacity of the resulting exchange material.

An interesting fact is the variation in the amount of sulfur introduced into the final exchange substance with increase in temperature of sulfonation. As shown in Tables 10, 11, 12, and 13 the sulfur content reached a maximum percentage at some point between 80° and 100° C. To further illustrate this fact the sulfur content and the temperature of sulfonation of samples from Tables 10, 11, and 12 are plotted in Figure 6. It is readily apparent that more highly concentrated acids introduce a greater percentage of sulfur than do lower concentrated acids. The reason for the increase in the amount of sulfur introduced as the temperature of sulfonation was elevated is easily recognized, but the exact reason for the drop in sulfur content above the critical temperature is not clear. It was observed during the sulfonation step that at temperatures above 85° C. increasingly larger amounts of sulfur dioxide were given off as the temperature was increased. This indicates that oxidation is taking place.

During the early stages of this investigation it was believed that the sulfonic acid group was introduced into the lignin molecule and that it was the exchangeable hydrogen of this group that was responsible for the exchange properties of the sulfonated lignin. The fallacy is apparent when Table 14 or Figure 7 are studied. The calculated values for the exchange capacity, in grains per pound, are obtained from the data given in Table 10 for Meadol sulfonated with concentrated or 93.2 per cent sulfuric acid and are based on the assumption that all of the sulfur present is in the form of a sulfonic acid radical, i.e., as LSO_3H, where L is used

FIGURE 6

EFFECT OF ACID CONCENTRATION AND TEMPERATURE ON THE SULFUR CONTENT OF SULFONATED MEADOL



to represent the lignin molecule. As usual the results are calculated as calcium carbonate equivalent.

Table 14

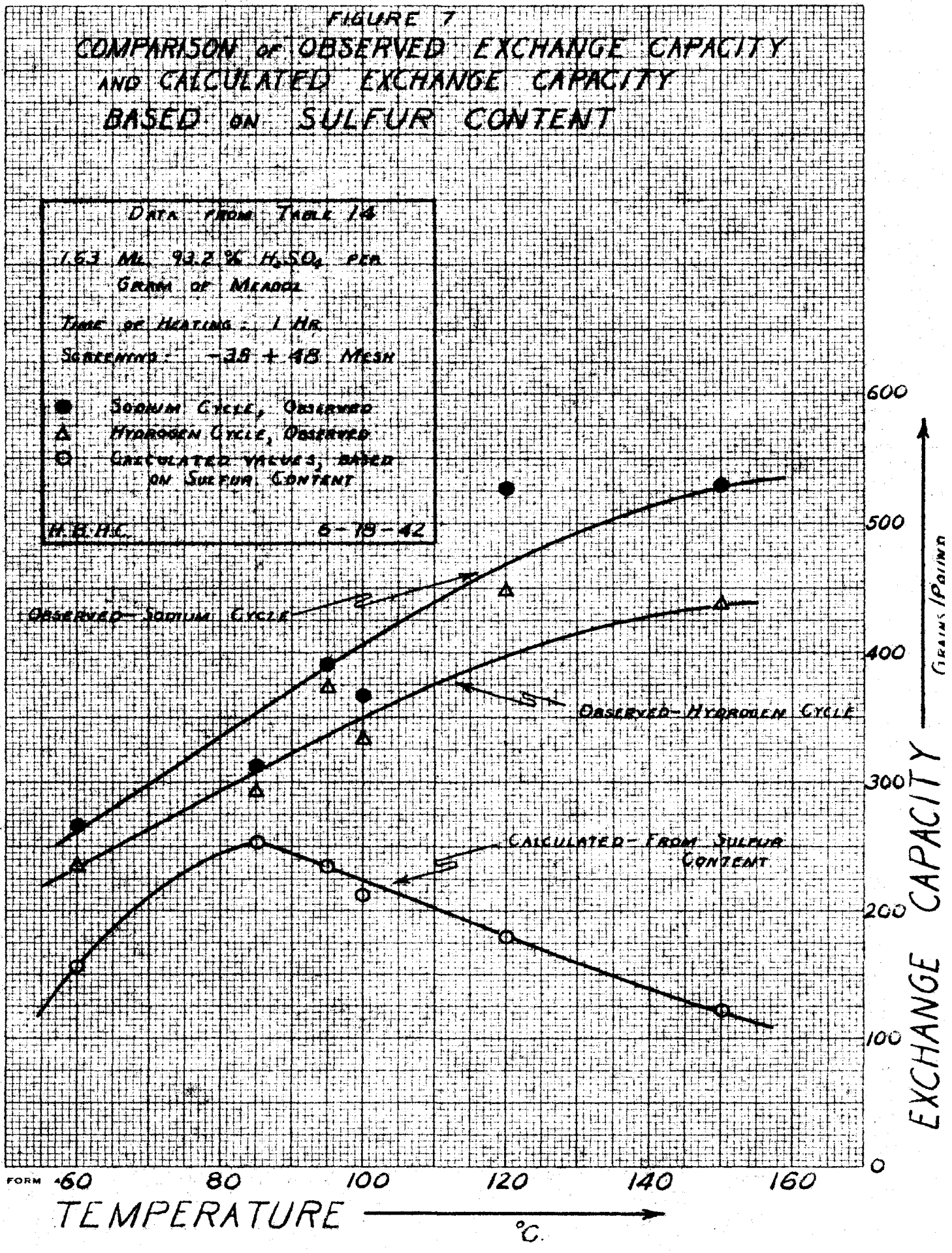
Comparison of Exchange Capacity Calculated from Sulfur Content and the Observed Exchange Capacity
(Data from Table 10)

Sample No.	Sulfonation Temperature °C.	Screening Mesh	Capacity Observed Grains per Lb. H^+	Capacity Observed Grains per Lb. Na^+	Per Cent Sulfur	Capacity Calculated from Sulfur Content Grains per Lb.
1	60	-10+20	269	269		
		-20+35	280	260		
		-35+48	237	267	1.43	156
2	85	-10+20	293	308		
		-20+35	271	287		
		-35+48	294	313	2.30	251
3	95	-10+20	218	235		
		-20+35	279	312		
		-35+48	374	391	2.15	235
4	100	-10+20	295	207		
		-20+35	275	295		
		-35+48	335	367	1.94	212
5	120	-10+20	251	251		
		-20+35	377	448		
		-35+48	448	527	1.65	180
6	150	-10+20	142	237		
		-20+35	387	592		
		-35+48	438	525	1.12	122

When Figure 7 is observed, it becomes apparent immediately that the replaceable hydrogen of the sulfonic acid group of the sulfonated lignin cannot alone be responsible for the observed exchange capacity. In addition, the calculated values assume that all sulfonic acid groups present

FIGURE 7

COMPARISON of OBSERVED EXCHANGE CAPACITY AND CALCULATED EXCHANGE CAPACITY BASED on SULFUR CONTENT



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are available for ionic exchange. Actually this is unlikely, since a large proportion of the groups would not be present on the surface to take part in the exchange cycle. The calculated values, therefore, represent a maximum rather than a probable value. As has been mentioned previously, there were indications that at temperatures above 85° C. sulfuric acid became increasingly more oxidizing in action. The oxidation of the lignin probably produced carboxyl, hydroxyl, and phenol groups which with their exchangeable hydrogens could account for the increase in exchange capacity. Thus the lignin exchange materials apparently were becoming somewhat similar to the humic acid exchange substances, the exchange properties of which are believed due to carboxyl groups (135). An additional factor supporting this conclusion is that humic acids are widely believed to be formed from lignin (51). In any event, higher temperature sulfonation increased the exchange capacity, whether due to the formation of additional carboxyl groups or to some form of surface activation. Activated carbons prepared at higher temperatures show greater adsorptive powers than when prepared at lower temperatures. Meadol alone, previous to sulfonation, did not show exchange properties.

Tables 10, 11, 12, and 13 show that exchange materials of greatest density are formed at sulfonation temperatures below 100° C., with some indications that sulfonated Meadol products prepared at approximately 90° C. possess greatest densities. On the other hand, exchange materials prepared at temperatures above 100° C. are porous and of very low density. Exchange materials of fairly high density are desirable in order to prevent their being carried away and subsequently being lost if upflow operation is used or during the backwashing stage in the case of downflow operation. Samples

prepared at a sulfonation temperature of approximately 95° C. showed a dry density of from 35 to 45 pounds per cubic foot. These densities are of similar magnitude to those of commercially used base-exchange materials, as is shown by reference to Table 6.

A very important property of an ionic exchange material is that it should not color the water being softened. Samples prepared at 85° C. or less showed a tendency to color the effluent when operated on the sodium cycle. On the hydrogen cycle the color "throwing" tendency was very much reduced and was largely limited to coloring the water that had stood in contact with the exchange material over a period of several days. As soon as this water passed on the discharged effluent became clear and colorless. Much less tendency to impart color was noted once the exchange materials had gelled. Definite gelling occurred with acid of 93.2 per cent or stronger at the acid lignin ratios used for all temperatures above 85° C. if heated for a sufficient period of time, usually less than two hours. Sulfonation temperatures higher than 100° C. gave samples which showed no tendency to color the water even when allowed to stand in contact over long periods of time. Higher temperatures, unfortunately, gave materials of low exchange capacity on the volume basis.

From an economic point of view it is advisable to produce a material of high exchange capacity, but even this property must be sacrificed to obtain a softened water with satisfactory color characteristics. Since a maximum volumetric exchange capacity, a high density product, and a substance with very little or no tendency to color the softened water were obtained when a sulfonation temperature of 95° C. was used, it was decided to investigate the effect of using high ratios of sulfonating acid to Neadol

at this temperature. Accordingly, exchange materials were prepared under these conditions, the results of which are shown in Tables 15 and 16.

Table 15 shows the results obtained by increasing the ratio of concentrated sulfuric acid to lignin. At high ratios the materials produced were of high exchange capacity and compared favorably with commercial exchange materials now being marketed. High densities and satisfactory stability, both in regard to solubility and color "throwing" when in operation over a period of continued operation for several weeks characterized Samples 27 and 32. The percentage of sulfur introduced increases gradually with higher ratios of acid to Meadol. Much higher ratios of concentrated acid to Meadol than 5:1 were not practical for producing cationic exchange materials under the conditions used, since a definite gel did not form readily. When water was added to cause the usual setting and stiffening of the gel only a black powdered material was produced.

At low ratios of acid to Meadol the exchange capacity on the sodium cycle was higher than that on the hydrogen cycle, but at high ratios the above condition was reversed.

Table 16 contrasts the results obtained when acids of varying concentration at 4.33 milliliters per gram of Meadol were used. Higher concentration acids increase the exchange capacity, as well as the sulfur content. There were indications that the strongest acid used, 20 per cent free sulfur trioxide sulfuric acid, produced materials which gave a softened water with even more satisfactory color characteristics than that discharged by materials prepared from concentrated sulfuric acid. Higher strength acids also cause some decrease in the density. This latter fact is probably due to the fact that gelling occurred while sulfur dioxide was still being

Table 15

Effect of Varying Ratio of Sulfonating Acid to Meadol

Concentration of Sulfuric Acid Used = 93.2 Per Cent H_2SO_4
Sulfonation Temperature = 95° C.

Sample No.	Time of Heating Hr.	Ratio of Acid to Meadol ml. per Gram	Particle Size Screening	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
3	1	1.63	-10+20	34.0	218	235	4720	5150	
			-20+35	37.9	279	312	6330	7080	
			-35+48	37.4	374	391	8870	9280	2.15
17	2	2.17	-10+20	39.4	334	351	6940	7290	
			-20+35	38.1	341	341	7020	7020	
			-35+48	42.1	384	401	8200	8570	2.57
27	2	4.33	-10+20	46.3	370	321	9560	8310	
			-20+35	45.6	452	452	9670	9670	
			-35+48	42.6	492	433	11970	10570	2.84
32	2	5.0	-10+20	44.3	469	402	9710	8320	
			-20+35	43.9	560	464	13080	10800	
			-35+48	44.4	602	521	13790	11920	2.97

Table 16

Effect of Concentration of Sulfonating Acid

Ratio of Sulfuric Acid to Meadol = 4.33 ml. H_2SO_4 per 1 Gram of Meadol
Sulfonation Temperature = 95° C.

Sample No.	Time of Heating Hr.	Sulfonating Acid	Particle Size Screening	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
27	1	93.2% H_2SO_4	-10+20	46.3	370	321	9560	8310	
			-20+35	45.6	452	452	9670	9670	
			-35+48	42.6	492	433	11970	10570	2.84
26	2	93.2% H_2SO_4	-10+20	46.0	310	296	8320	7940	
			-20+35	47.5	355	369	9050	9410	
			-35+48	48.1	400	400	9830	9830	2.83
28	2	99% H_2SO_4	-10+20	42.6	285	342	6760	8100	
			-20+35	44.8	397	461	10220	11850	
			-35+48	42.5	485	519	10810	11540	3.43
29	2	20% Fuming or 104.5% H_2SO_4	-10+20	37.9	355	371	7500	7850	
			-20+35	40.4	443	443	10210	10210	
			-35+48	39.9	549	511	11850	11030	4.13

evolved rapidly, within approximately 15 minutes. As a result large amounts of gas were trapped within the gel, thus giving a more porous structure with a resulting decrease in density. In addition, fuming sulfuric acid is more strongly oxidizing at a given temperature than are the more dilute acids, thus causing the evolution of somewhat larger quantities of sulfur dioxide.

Complete data were not obtained regarding the yields of the sulfonated Meadol exchange product, but the incomplete data indicated that yields of between 80 and 98 per cent, dry basis, were obtained. Yields on the low side of this range were obtained for samples prepared at high acid to lignin ratios, except where the more concentrated sulfonating acids were used.

Because of the close similarity in behavior between Meadol and lignin recovered from the alkaline cornstalk cook liquors, this latter type of lignin was sulfonated only at a high ratio of ordinary concentrated sulfuric acid to lignin at 95° C. The very high exchange capacities obtained, as shown in Table 17, indicated that the alkali type cornstalk lignin gives a material that is slightly superior in this property to corresponding products obtained from Meadol, as well as being equal to or superior to the principal commercial exchange materials available in this country, e.g., Amberlite IR-1, Zeokarb Na^+ or H^+, and Nalcite "AX." The exchange capacities of these latter materials are tabulated in Table 2. The density of the product was high, varying between 46 and 48 pounds per cubic foot.

A disadvantage of the product from this type of lignin is the slight tendency for the water being softened to become somewhat colored when allowed to stand in contact with the exchange material when operated on the sodium cycle. On the hydrogen cycle this difficulty was very much decreased and

was only very slightly noticed. Even with the commercial types of exchange materials, some tendency to color water being softened exists and it is recommended that the exchange materials should not be used for intermittent operation. The following is quoted from operating instructions (108) for Amberlite IR-1:

> Because Amberlite IR-1, especially in the preliminary cycles, tends to impart some color to the effluent when used in discontinuous operation, it is not recommended that the product be used for domestic units, or in other specialized fields wherein intermittent use is required.

Table 17

Exchange Material Prepared from Cornstalk Soda Lignin

Ratio of sulfuric acid to lignin = 4.33 ml. of 93.2% H_2SO_4 per gram of lignin
Sulfonation temperature = 95° C.
Time of heating = 2 hours

Particle Size Screening	Density Dry Lb. per Cu. Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu. Ft. Wet Packed H^+	Capacity Grains per Cu. Ft. Wet Packed Na^+	Per Cent Sulfur
-10+20	46.2	495	495	11130	11130	
-20+35	46.9	669	621	15980	14810	
-35+48	48.1	764	636	17620	14700	5.32

An interesting fact is that the sulfur content is nearly double that of the exchange material prepared from Meadol under the same conditions. It seems probable that the increased amount of sulfur introduced should have much to do with the increased capacity. Bridger (21) observed that a higher percentage of lignin was obtained when lignin was precipitated with a strong acid, such as hydrochloric acid, than when precipitated with carbon dioxide. Bridger also concluded that this fraction precipitated by

the strong acid but not by carbon dioxide differed chemically from the carbon dioxide precipitated fraction. If so, perhaps this additional fraction might be responsible for the fact that an additional amount of sulfur was introduced. Continuing to speculate, another explanation might be that lignin isolated from straws and stalks yields a higher ratio of vanillin to syringaldehyde than does lignin from woody materials, such as: spruce wood, maple wood, and aspen wood (71). As mentioned previously, Hibbert and co-workers (71) are of the opinion that α-hydroxypropiovanillone and α-hydroxypropiosyringone condense together to yield lignin. A higher ratio of the vanilloyl radical, such as occurs in lignin from straws and stalks might possibly allow sulfonation to proceed to a greater extent, since an additional position is available for substitution in the aromatic nucleus of the vanilloyl group, than in the syringoyl group. In any event, the higher exchange capacity and the higher percentage of sulfur of the cornstalk lignin product than for the corresponding product from Meadol indicate that some difference exists between Meadol and the lignin material obtained from cornstalks.

Table 18, which appears on the following page, summarizes the results obtained by sulfonating the furfural oat hull residue and the Klason type of lignin also obtained from this source. The exchange materials prepared differed from corresponding materials prepared from Meadol and the alkali type of cornstalk lignin used in that at no time did solution or gelling occur. Even after the sulfonation treatment the original oat hull structure was much preserved. The density of the resulting materials was low, being very much lower than the products prepared from Meadol under the same conditions. Increased concentration of sulfonating acids used produced

Table 18

Exchange Materials from Furfural Oat Hull Residue

Ratio of Sulfuric Acid to Material Sulfonated = 6.5 ml. Acid per Gram of Material
Time of Heating = 2 hr.
Sulfonation Temperature = 95° C.

Sample No.	Material Sulfonated	Sulfonating Acid	Particle Size	Density Dry Lb. per Cu.Ft.	Capacity Grains per Lb. Dry Basis H^+	Capacity Grains per Lb. Dry Basis Na^+	Capacity Grains per Cu.Ft. Wet Packed H^+	Capacity Grains per Cu.Ft. Wet Packed Na^+	Per Cent Sulfur
30	Oat hull furfural residue	93.2% H_2SO_4	-10+20	21.7	241	241	3270	3270	
			-20+35	23.1	411	383	6020	5710	
			-35+48	22.5	468	390	7020	5840	2.61
20	Lignin from oat hull furfural residue (Klason type)	Not sulfonated	-10+20	12.9	0	0	0	0	
			-20+35	12.1	0	0	0	0	
			-35+48	12.0	0	0	0	0	0.42
21	Lignin from oat hull furfural residue (Klason type)	93.2% H_2SO_4	-10+20	18.9	409	520	3980	3620	
			-20+35	16.3	500	637	4030	5140	
			-35+48	16.9	632	675	6230	6650	2.20
22	Lignin from oat hull furfural residue (Klason type)	99% H_2SO_4	-10+20	22.5	688	563	8190	6700	
			-20+35	20.2	758	682	8570	7830	
			-35+48	19.0	845	803	8450	8030	4.35
23	Lignin from oat hull furfural residue (Klason type)	20% SO_3 fuming 104.5% H_2SO_4	-10+20	22.8	763	564	9560	7060	
			-20+35	21.8	829	663	8820	7050	
			-35+48	19.1	1098	806	10570	7740	5.25

increased exchange capacity, both on the weight and on the volume basis. In addition, increased acid strength increased the amount of sulfur in the resulting products. No exchange properties were noted with the Klason lignin alone, even though a small amount of sulfur was found to be present. The sulfur may have been present in the original inorganic skeletal structure of the furfural oat hull residue or, more likely, it may have been introduced during the hydrolysis of the carbohydrate materials with the 72 per cent sulfuric acid used during the lignin isolation step. Samples prepared from the lignin material alone possessed bad color "throwing" properties and this difficulty seemed to increase when stronger sulfonating acids were used. Oddly enough, Sample 30, prepared from the original furfural oat hull residue alone, possessed much better properties in this respect and colored the water only very slightly.

Because of the high color "throwing" tendency and the very low density of exchange materials produced, this source of raw material does not seem particularly promising for use in preparing cationic exchange substances unless a further method of treatment leading to color "stabilization" is found.

6. Discussion

It is of interest to note that it is apparently the lignin or closely related materials which make it possible for materials of vegetable origin to exhibit exchange properties. All organic components of plant substances cannot be made to exhibit this property. Supporting the above conclusion are the results of Burrell (25) who reported that cellulose and cane sugar were completely inactive when heated and only slightly active when carbonized

with sulfuric acid. In addition, Columbia carbon and coconut activated carbon did not exchange for calcium or magnesium, nor did they do so after being treated with concentrated sulfuric acid. Burrell further reported that exchange materials could be prepared from the catechol but not the pyrogallol type of tannin extractive from plant materials upon treatment with sulfuric acid. Reti (128) states that the formation or synthesis of aromatic materials within plants, which includes the tannin materials mentioned above, merely represents ramifications of the principal synthesis taking place which is the formation of lignin. Whether the principal remaining component in the plant material, the hemicelluloses, can be made to exhibit base-exchange is not known; but it seems plausible that it would behave in a manner similar to the cellulose, since both are closely related structurally and chemically. It has been noted in this laboratory, however, that furfural, a product obtained from the hemicelluloses, can be made to show exchange properties when treated with concentrated sulfuric acid. In any event, sulfonation is necessary to bring about exchange properties, since neither Meadol nor Klason lignin from the furfural oat hull residue showed this property previous to sulfonation.

7. Commercial production

In order to estimate the cost of raw materials required to prepare a cationic exchange material from Meadol, it is necessary to select a product with desirable properties. As has been mentioned previously, it is possible to prepare exchange materials with a wide variety of physical and chemical properties. Among the factors to be considered are: high exchange capacity, stability to the action of aggressive waters, satisfactory color "throwing"

characteristics, high density, high yield of product, ease of production and low ratio of sulfuric acid to Meadol. After consideration of the various exchange materials prepared, it appeared that Sample 28 was most satisfactory from the standpoint of the above factors. Table 19, which appears below, summarizes the necessary information regarding Sample 28.

Table 19

Exchange Material Prepared from Meadol with Desirable Qualities

(Sample 28)

Temperature of sulfonation	**= 95° C.**
Ml. of acid per gram of Meadol	**= 4.33 : 1**
Concentration of sulfuric acid	**= 99%**
Time of heating	= 2 hr.
Time before gelling	= 1 hr. 20 min.
Yield of product, dry basis	**= 94%**

	Particle Size Screening		
	-10+20	-20+35	-35+48
Density, dry, lb. per cu. ft.	42.6	44.8	42.5
Capacity, grains per lb.			
Hydrogen cycle	285	397	485
Sodium cycle	**342**	**461**	**519**
Capacity, grains per cu. ft.			
Hydrogen cycle	**6760**	**10220**	**10810**
Sodium cycle	8100	11850	11540
Per cent sulfur			3.43

The expected exchange capacity of the above exchange material, as furnished, would probably vary between 10,000 and 11,000 grains per cubic foot. This result is probably on the conservative side since, at an earlier date, a sample had been prepared with the same concentration of sulfonating acid and at the same ratio of acid to Meadol but with only an approximate

control of the temperature at 95° C. This sample showed exchange capacities of approximately 10,000 grains per cubic foot for a passing 10 mesh retained on 14 mesh sample and 15,000 grains per cubic foot for a passing 14 mesh retained on 65 mesh sample. Sample 28 was tested continuously over a period of several weeks and was found to operate adequately and satisfactorily in every respect.

Two important factors should be considered before a product of this type can be marketed. These are: (1) whether the product can be manufactured successfully with ordinary or standard materials of construction and (2) whether the product can be produced at a price comparable to that of existing materials with similar properties.

a. Proposed process. The equipment necessary for producing cationic exchange materials, discovered in this investigation, on a commercial scale should present no great difficulties from a design, construction or corrosion standpoint. Figure 8 shows a proposed flow sheet for the process.

The sulfonator could be of the jacketed steel type, since sulfuric acid of the strength used does not readily attack steel. The use of water as a heating medium allows for the necessary flexibility of temperature control during the early stages of sulfonation when the reaction is exothermic. Since a temperature of 95° C. is sufficient for the preparation of the exchange material, no particular difficulty should be encountered with the use of hot water. Means should be provided for tilting the sulfonator in order to discharge the sulfonated lignin gel formed. In addition, a hood or means of removing the sulfur dioxide evolved should be provided.

The setting and washing trough used for the next step could be constructed of wood, but should be lined with lead, preferably a hardened lead,

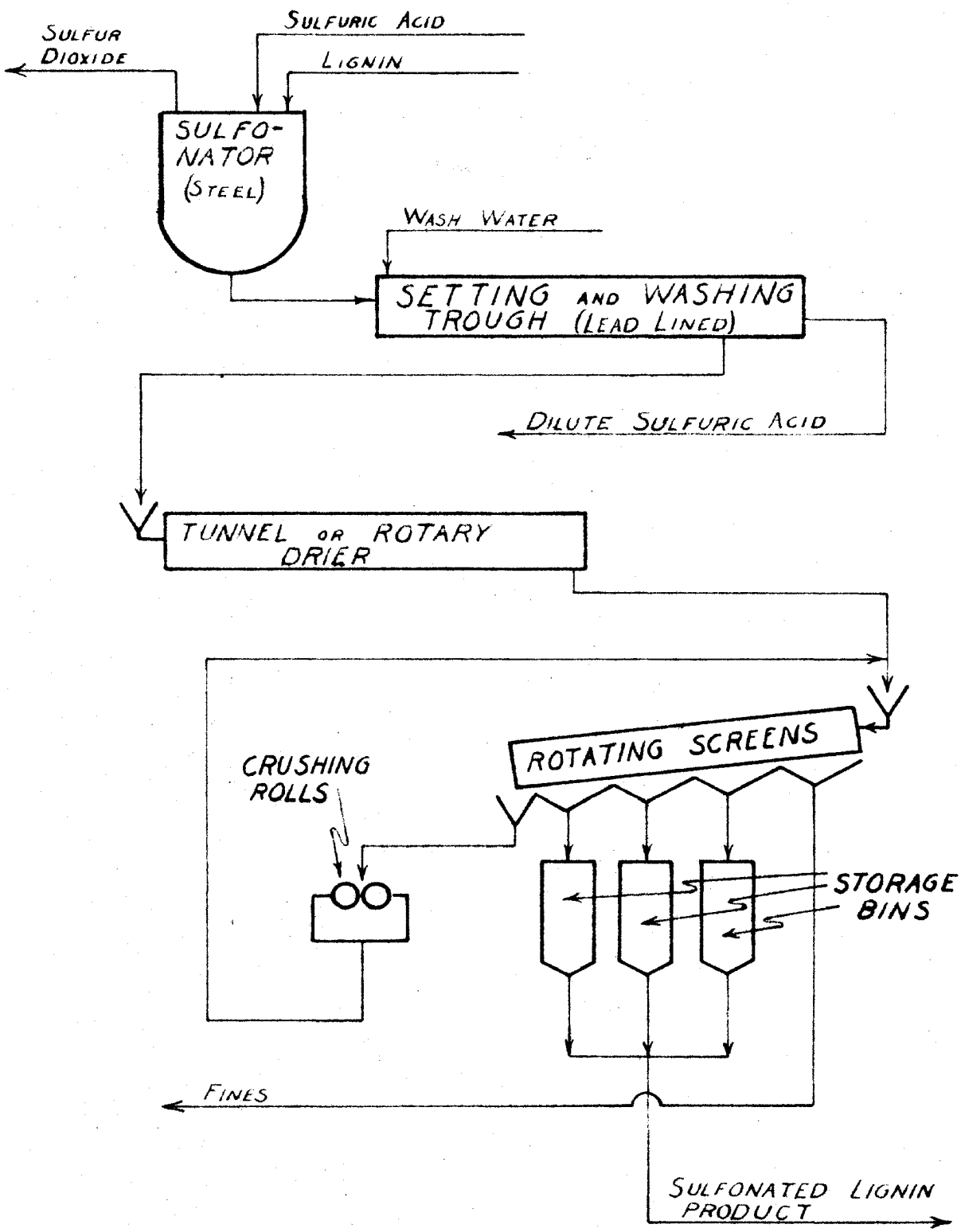


FIG. 8. PROPOSED PROCESS FOR MANUFACTURE OF SULFONATED LIGNIN CATIONIC EXCHANGE MATERIAL

such as the antimony lead type. This material is rigid and is equally resistant to dilute and strong sulfuric acid as is ordinary lead. The lead lined trough should be constructed in such a manner that the sulfonated lignin gel could be spread out to a thin layer in order to obtain a large amount of surface for the washing or acid leaching operation. This would require a series of shallow troughs, several feet in width and of whatever length would be necessary to provide space for the required amount of exchange material. Following the sulfonation step the partially gelled material could be poured out of the sulfonator onto the trough. The sulfonated product could either be spread by hand or it could be distributed by locating the troughs on rolls so that they could be passed beneath the sulfonator being discharged. Following a period of several hours during which time the gel would be allowed to set, the sulfonated lignin could then be washed by passing a shallow layer of water over the gel in the trough. This should be done intermittently at first with a short time between washings in order to allow hardening of the gel to take place as the sulfuric acid is removed. In addition, this permits obtaining a sulfuric acid of considerable strength during the first few washings. Later a continuous stream of water could be passed through the trough. The hardened gel could then be broken up by hand and after washing further could be transferred to a tunnel or rotary drier.

After the drying step the exchange material could then be screened to the desired size and transferred to storage. The oversize particles could be passed through rolls and be reduced to the required particle size range and then be repassed through the rotating screens. While not investigated thoroughly, there is some evidence that at least a portion of the fines could be added to the fresh material being sulfonated.

The process could be made essentially continuous after the washing step by use of conveyors. By operation of a number of the sulfonating and washing units discharging in a staggered manner it would be possible to simulate continuous operation.

The stronger sulfuric acid wash liquor obtained from the first few washings could be concentrated for reuse, while the dilute sulfuric acid from later washings could be used for obtaining other valuable products from woody or agricultural waste materials. Among these are furfural and xylose from the pentosans, or the cellulose could be hydrolyzed to produce soluble sugars which could then be fermented to alcohol, as is done in the Scholler-Tornesch process. In addition, a small amount of sulfuric acid is necessary in the production of Meadol to remove the last traces of alkali.

b. Cost of production. Before an accurate estimate of the total cost of preparing the cationic exchange material from Meadol could be made, it would be necessary to construct and operate a pilot plant. By making certain assumptions, however, which have been found to hold in the case of other chemical materials, an approximation of the final cost can be made.

For large scale operations where continuous operation is used, the cost of raw materials may amount to as much as 50 to 60 per cent of the final sale price. For processes requiring considerable direct labor or a large number of intermediate processing steps the raw material cost makes up approximately one third of the selling price. Accordingly, to be on the conservative side, a ratio of raw material cost to final price of 1 to 3 has been assumed.

The raw materials necessary are Meadol, 66° Baume sulfuric acid, and 20 per cent sulfur trioxide oleum. Meadol is now sold at a price of 6 cents per pound, but in view of the fact that this price includes profit and because Meadol is now produced only in a small pilot plant, it is felt that 2 cents per pound is a more probable figure. Current price quotations list 66° Baume sulfuric acid at $16.50 per ton, 20 per cent sulfur trioxide oleum at $19.00 per ton and 60° Baume sulfuric acid at $13.00 per ton.

In the following calculations regarding the cost of the cationic exchange material produced from Meadol three cases have been considered. These are:

Case 1. Meadol costs 6 cents per pound and no sulfuric acid is recovered.

Case 2. Meadol costs 2 cents per pound and no sulfuric acid is recovered.

Case 3. Meadol costs 2 cents per pound and 50 per cent of the sulfuric acid is recovered.

The calculations are based on the data obtained in the preparation of Sample 28 shown in Table 19.

The calculations show that exchange materials manufactured under the assumptions of Case 2 and Case 3 can definitely compete with commercial cationic exchange materials now being marketed. It was impossible to obtain price quotations on either Zeokarb Na^+ or H^+, or Nalcite "AX," but a price of 31 cents per pound was quoted (38) for Amberlite IR-1. Since Amberlite IR-1 competes with the other products mentioned, it is reasonable to assume that their selling prices are comparable. It is believed that the assumptions of Case 3 could be realized and as a result that the manufacture of a cationic exchange material from Meadol is definitely feasible commercially.

Cost of Producing Cationic Exchange Material from Meadol

Basis = 100 Pounds of Product

Materials required

Meadol (94% yield) = 100/0.94 = 106.5 lb.
66° Be' H_2SO_4 = (2.165)(1.84)(106.5) = 424 lb.
20% SO_3 Oleum = (2.165)(1.88)(106.5) = 434 lb.

Cost of materials

Case 1
Meadol = (106.5)(0.06) = $6.39
66° Be' H_2SO_4 = (424)(16.50/2000) = $3.50
20% SO_3 Oleum = (434)(19.00/2000) = $4.12 $7.62
Total cost per 100 pounds of product = $14.01

Case 2
Meadol = (106.5)(0.02) = $2.13
Sulfuric acids = $7.62
Total cost per 100 pounds of product = $ 9.75

Case 3
Meadol = $2.13
Sulfuric acids = $7.62 $9.75

Sulfuric acid recovered (50% recovery calculated as 60° Be' H_2SO_4) =
(424 + 434)(.99)(.50)/.7767 = 547 lb.

Value of recovered acid = 547(13.00/2000) = $3.56
Cost of materials = $ 6.19

Selling price of product

For Case 1 14.01/0.3333 = $42.0 per 100 pounds of product

For Case 2 9.75/0.3333 = $29.2 per 100 pounds of product

For Case 3 6.19/0.3333 = $18.6 per 100 pounds of product

B. Anionic Exchange Substances

In general, high molecular weight bodies tend to be insoluble in water, even when certain groups are present which tend to promote water solubility. Since lignin is a body of high molecular weight, it seemed plausible that anionic exchange materials could be prepared by attaching basic groups, e.g., the amine group. Accordingly, lignin was aminated. The resulting aminated lignin was found to possess acid exchange properties. The aminated lignin material was prepared by first chlorinating Meadol and then reacting the chlorinated lignin product with ammonia under pressure at elevated temperatures according to the following reactions:

$$L \xrightarrow{\text{Chlorination}} L.Cl \xrightarrow{\text{Amination}} L.NH_2$$

L = Lignin molecule

The ammoniacal solution of the aminated lignin was neutralized with hydrochloric acid, whereupon the aminated lignin precipitated. The precipitate was then filtered, washed and dried.

Following a similar line of reasoning to that employed in the first paragraph of this section, any increase in the molecular weight of the aminated lignin material should result in a product of even lower water solubility. With this in mind, an effort was made to bring about a condensation reaction between aminated lignin and formaldehyde. The resulting product showed little evidence that the desired condensation reaction had taken place, but the product still showed similar acid exchange properties to the original aminated Meadol alone.

In addition to the above two types of exchange materials, a third type

was prepared by reacting chlorinated Meadol and aniline. A hard black resinous material was formed, but unfortunately anionic exchange properties were not exhibited.

1. Materials used

The raw materials used were anhydrous chlorine, 28 per cent aqueous ammonia, aniline, 40 per cent formaldehyde, and Meadol. Meadol, as described earlier, is an alkali type lignin product precipitated from spent liquors of the soda paper pulping process by carbon dioxide. The Meade Paper Company of Chillicothe, Ohio provided the Meadol.

2. Preparation of intermediate materials

a. Chlorination. The reaction of chlorine with lignin in aqueous suspension proceeds readily at atmospheric pressure if a large enough contact surface can be provided. Unfortunately, bubbling chlorine through a suspension of Meadol in water was inadequate, since large amounts of chlorine escaped to the surroundings. As a result it was found necessary to devise some means of overcoming this difficulty. Accordingly, a device was developed which was satisfactory to a large extent.

Figure 9 illustrates the apparatus constructed. The chlorine gas passed into the off-run connection of the glass T and then on down around the revolving shaft of the glass stirring rod. The shaft was sufficiently small and the internal diameter of the T was large enough to allow ready passage of the gas. A rubber tubing seal on the top end of the T, lubricated with glycerine, fitted around the rotating shaft and prevented discharge of the chlorine to the atmosphere. The chlorine gas passed down the glass T

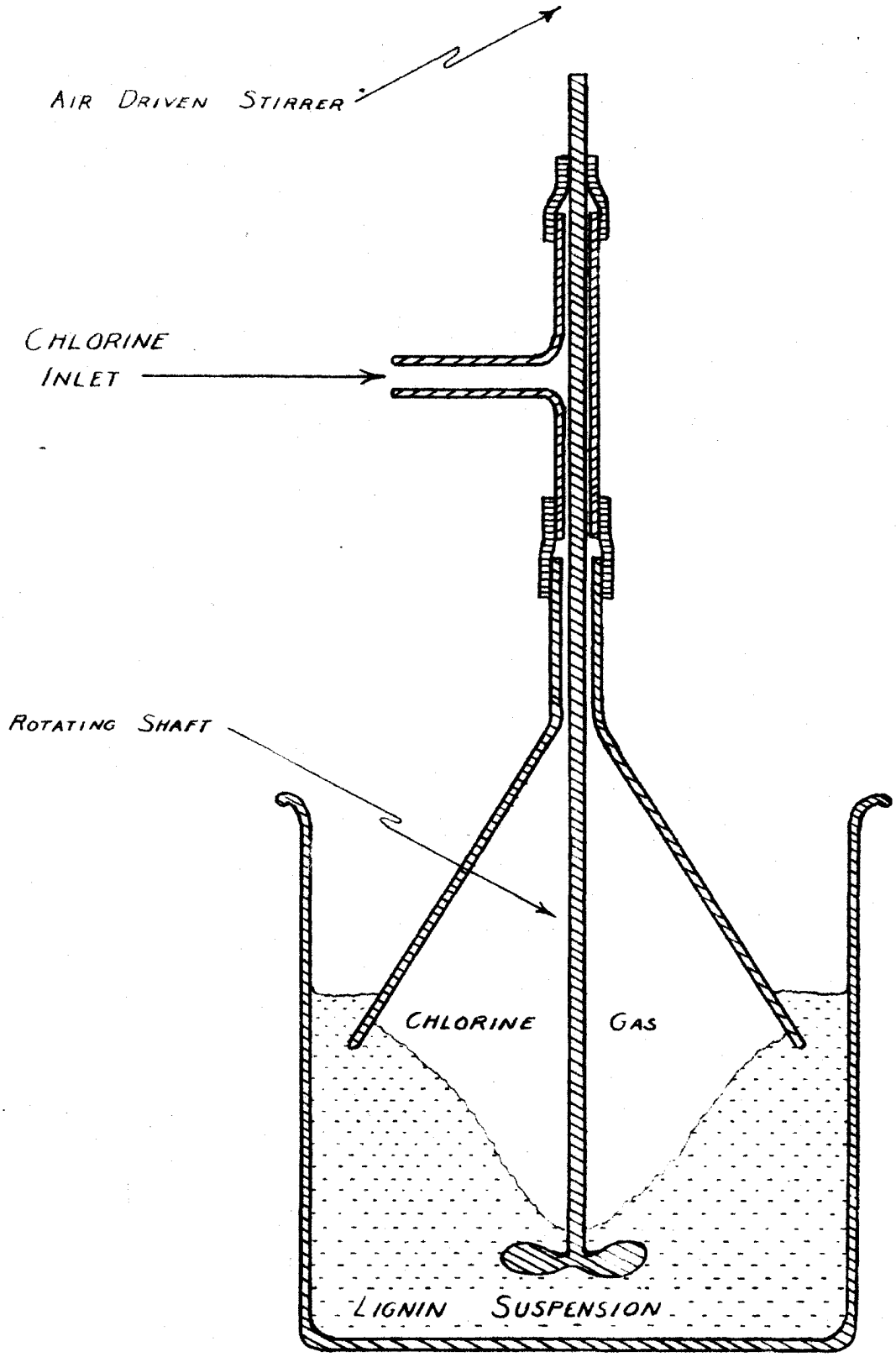


FIG. 9. CHLORINATION APPARATUS

into an inverted funnel. The bottom edge of the funnel projected approximately one half inch below the surface of the aqueous lignin suspension in a one liter beaker. The propeller on the stirring rod kept the suspension well agitated at all times, thereby bringing fresh liquid and lignin to the surface to contact the chlorine in the cone of the funnel. The reaction proceeded fairly rapidly and little difficulty was experienced with chlorine escaping to the surroundings. The rate of chlorine admission was adjusted to the highest rate possible so that no chlorine bubbled out to the atmosphere from under the funnel. Usually eight hours were sufficient to saturate the lignin to the point where no more chlorine was taken up. The rate of chlorine flow was checked with a bubble counter previous to entrance into the chlorination apparatus. The bubble counter was made from a 500 milliliter wide mouth bottle fitted with a two-hole rubber stopper.

Four hundred grams of Meadol were suspended in about 600 milliliters of water. If a larger amount of lignin was used the resulting suspension was too thick to be mixed easily by the air driven stirrer. After chlorination the chlorinated lignin was filtered, washed with water and dried on a steam plate. Ten milliliters of a 5 per cent ferric chloride solution were added to the Meadol suspension during chlorination in order to catalyze the substitution reaction of the chlorine into the aromatic nuclei of the lignin as much as possible. The reasoning behind the desire to promote the substitution of chlorine atoms into the aromatic nuclei of the lignin to a high extent was that ultimately the substituted chlorine atoms were to be replaced by amine groups. Amine groups attached directly to an aromatic nucleus are much more firmly held and less easily hydrolyzed away than are amine groups attached to aliphatic groups. Firmly held amine groups

would be a necessary property of a material to be used as an anionic exchanger. Based on the original lignin a yield of approximately 95 per cent of chlorinated lignin was obtained.

b. Amination. The chlorinated Meadol was ammoniated in a 5 liter vertical type hand-stirred high pressure steel autoclave. Three hundred grams of chlorinated Meadol were added to 2500 milliliters of 28 per cent aqueous ammonia. In order to catalyze the substitution reaction of amine groups for chlorine atoms present in the chlorinated lignin 10 grams of cuprous chloride were added. The contents were then heated to a temperature of 140° C. and a corresponding pressure of 230 pounds per square inch. The autoclave was heated for 3 hours under these conditions, being stirred constantly. At the end of this heating period the mixture was allowed to cool to room temperature and was then removed.

The ammoniacal liquors and a slight amount of insoluble black residue were then acidified with concentrated hydrochloric acid until the end point to litmus was reached. Shortly before arriving at this stage a large amount of aminated lignin was precipitated. The precipitate filtered readily through a Buchner filter giving a clear filtrate. The aminated lignin was washed thoroughly to remove any ammonium chloride and it was then dried on a steam plate. The yield of aminated lignin based on chlorinated lignin was 85 per cent.

3. Preparation of exchange samples

a. Aminated Meadol. The aminated lignin precipitate was obtained in the form of a fine amorphous black powder and thus was not satisfactory for use directly as an exchange material. While investigating the use of

aminated lignin as a plastic material it had previously been noted that this type of lignin could be molded. Although not possessing enough strength for use as a plastic, the structure of the molded material was entirely satisfactory for use as an exchange material when broken down and graded to the proper particle size distribution.

The dried aminated lignin was placed in a cylindrically shaped steel mold having a cross-sectional area of one square inch. Ten grams of material were placed in the mold. The mold was then placed in the molding machine and was heated to a temperature of 110° C. with an applied pressure of 5000 pounds per square inch. Ten of the molded disks provided a sufficient amount of the exchange material for the tests conducted.

After molding, the disks were crushed with a mortar and pestle. The crushed material was then screened with Tyler Standard sieves. Two fractions were collected: passing 10 mesh retained on 20 mesh, and passing 20 mesh retained on 48 mesh. The individual particles were hard, black and somewhat resinous in appearance.

The sieved samples were then packed wet in glass tubes in a manner similar to that used with the cationic exchange materials after swelling the samples in water. The exchange material was washed thoroughly while in the tube with ordinary tap water in order to remove any soluble material. A slight amount of brownish color appeared in the first wash water, but the color disappeared after a few minutes.

b. Aminated Meadol-formaldehyde product. A one gallon cast iron fusion kettle, fitted with a removable cover, a hand stirrer, and a glass reflux condenser, was used as a reaction vessel. The fusion kettle was placed in an oil bath held at 125° C. A mixture of 200 grams of aminated

Meadol, 400 milliliters of 40 per cent formaldehyde, 5 grams of hexamethylene tetramine and 20 grams of calcium hydroxide was heated in the vessel at 100° C. for approximately 3 hours. The mass stirred easily during the period of heating. Following this a vacuum was drawn on the vessel to remove water and unreacted formaldehyde. The contents of the vessel were then discharged. No resinification was observed to have taken place and the contents appeared to be much the same as before. A yield of 295 grams of dried product was obtained.

The aminated Meadol-formaldehyde product was then molded and reduced to the desired particle size in a manner similar to that used in the preceding section for the preparation of the aminated Meadol samples.

c. Chlorinate Meadol-aniline product. Three hundred grams of chlorinated Meadol and 200 grams of aniline were heated together at 110° C. for one hour in a one gallon cast iron fusion pot. The vessel was fitted with a removable cover, a hand stirrer, and a glass reflux condenser. An oil bath, heated to 130° C., kept the reaction vessel at the desired temperature. During the early stages the mass was quite plastic and stirred easily, but it became considerably stiffer as time progressed. At the end of the heating period the mixture was removed and placed in an iron pan to harden. The resulting product was glistening and black in appearance. A faint odor of aniline could be detected. The material was thermoplastic; it hardened readily on cooling to room temperature. A yield of 490 grams of product was obtained.

The aniline-chlorinated Meadol product was broken into small pieces by hand and was then crushed to the required particle size range with a mortar and pestle. The finely divided material was then screened to the

desired size distribution. Two samples were collected: passing 10 mesh retained on 20 mesh and passing 20 mesh retained on 48 mesh.

4. Testing of exchange materials

In order to test the anionic exchange materials made, it was necessary to prepare an artificially acidified water of known strength. A hydrochloric acid solution 27.5 grains per gallon, expressed in terms of calcium carbonate equivalent, was made up by diluting 0.1 N hydrochloric acid to the desired value with distilled water. The deacidified effluent from the test samples was tested every 100 milliliters discharged by titrating with 0.04 N sodium hydroxide solution to a phenolphthalein endpoint.

Downflow operation was used and a flow rate of approximately 20 milliliters per minute was maintained when removing acid. When regenerating, a flow rate of 5 milliliters per minute was used. Previous to testing for exchange capacity 100 milliliters of distilled water was passed through the exchange material so as to flush out any remaining alkaline regenerating solution. Various regenerating solutions were used. Among these were: 5 per cent sodium bicarbonate, 2 per cent sodium carbonate, and 1/2 per cent sodium hydroxide. One hundred and fifty milliliters of sodium bicarbonate were used for regeneration for the quantitative tests shown in Table 20.

5. Results

The aminated lignin anionic exchange material prepared was effective as an acid adsorbent. A practically neutral effluent was discharged from the finer screened sample, passing 20 mesh retained on 48 mesh, as can be seen from the data presented in Table 20. With the larger average particle

size sample, passing 10 mesh retained on 20 mesh, there was a tendency to "leak" anions. In the case of this latter sample the increase in the acid concentration of the discharged effluent was gradual, whereas in the case of the finer graded sample the acid removal was practically complete until the break-through was reached, after which point the acid content of the discharged solution rose rapidly. As is also seen in Table 20 the degree of removal was approximately 99 per cent of the original acid present up to the break-through. Samples of a commercial anionic exchanger, Amberlite IR-4, gave an effluent of approximately the same acid concentration.

The exchange capacity of the finely divided sample, passing 20 mesh retained on 48 mesh, was found to be 3840 grains per cubic foot of aminated lignin calculated as the calcium carbonate equivalent. With the coarser graded samples, it was impossible to calculate the exchange capacity to the break-through since an acid free discharge was not obtained.

The data given in Table 20 are from typical runs. Four or five tests were made on each sample. In all cases the break-through and the degree of acid removal were, for all practical purposes, the same.

The effluent was clear and practically colorless except for a very slight pale yellowish color when the first deacidified water was discharged after regenerating and flushing.

The aminated lignin was not stable to regenerating solutions of high pH. A 1/2 per cent solution of sodium hydroxide and a 2 per cent solution of sodium carbonate were used for regeneration on the first few tests, but their use was discontinued because the discharged effluent was colored dark brown as it left the exchange tube. This indicated that the aminated lignin was being dissolved by the strong alkali. As a result, a 5 per cent

Table 20

Aminated Meadol Anionic Exchange Material

Passing 10 mesh retained on 20 mesh Volume of exchange material = 0.00180 cu. ft.			Passing 20 mesh retained on 48 mesh Volume of exchange material = 0.001872 cu. ft.		
Ml. of Effluent	Ml. of 0.04 N Sodium Hydroxide per 20 Ml. of Effluent	Grains per Gallon of Hydrochloric Acid, as Calcium Carbonate, in Effluent	Ml. of Effluent	Ml. of 0.04 N Sodium Hydroxide per 20 Ml. of Effluent	Grains per Gallon of Hydrochloric Acid, as Calcium Carbonate, in Effluent
100	0.5	2.92	100	0.05	0.29
200	0.5	2.92	200	0.05	0.29
300	0.2	1.17	300	0.05	0.29
400	0.2	1.17	400	0.05	0.29
500	0.5	2.92	500	0.05	0.29
600	0.8	4.68	600	0.05	0.29
700	1.0	5.85	700	0.05	0.29
800	1.1	6.43	800	0.05	0.29
900	1.1	6.43	900	0.05	0.29
1000	1.0	5.85	1000	0.10	0.58
1100	1.25	7.31	1100	0.20	1.17
1200	1.1	6.43	1200	0.30	1.76
1300	1.1	6.43	1300	0.70	4.09
1400	1.1	6.43	1400	1.60	9.35
1500	1.6	9.36	1500	2.30	13.46
1600	2.0	11.70			
1700	2.2	12.88			
1800	2.9	16.97			
1900	3.3	19.30			
2000	3.5	20.47			

Acid feed solution required 4.7 ml. of 0.04 N sodium hydroxide per 20 ml. sample. This represented an initial hydrochloric acid concentration of 27.5 grains per gallon, as calcium carbonate.

solution of sodium bicarbonate was then used. This latter was found to be fairly satisfactory, however, the waste regenerating solution was still slightly colored. When regenerating with sodium hydroxide and sodium carbonate very large quantities of distilled water were necessary to flush out the residual alkali and give a clear effluent. With the use of sodium bicarbonate for this purpose, 100 milliliters of distilled water was usually sufficient to remove all but a trace of color. After operating a short time on the acid removal cycle, the remainder of the color disappeared.

The aminated Meadol-formaldehyde product had an exchange capacity of 2450 grains per cubic foot. The somewhat lower capacity than that of aminated Meadol alone is apparently due to some change brought about in the formaldehyde treatment, probably due to a slight amount of condensation which tended to eliminate some amine groups from acid exchange. Both the aminated Meadol and the aminated Meadol-formaldehyde product were very similar structually, thus tending to indicate that little condensation had taken place between molecules of the aminated Meadol. As can be seen from Table 21, the degree of removal was approximately the same as with aminated Meadol alone. The effluent or deacidified water had similar color characteristics, running very slightly colored for the first minute but clearing up shortly afterwards. Sodium hydroxide and sodium carbonate were observed to cause solution of the exchange material, while sodium bicarbonate appeared satisfactory in this respect.

The chlorinated Meadol-aniline product was tested for acid adsorptive properties. No significant amount of acid was removed from the standard hydrochloric acid test solution. The 2 per cent sodium carbonate regenerating solution tended to discolor badly, but the 5 per cent sodium bicarbonate

Table 21

Aminated Meadol-Formaldehyde Product

Passing 20 mesh retained on 48 mesh
Volume of exchange material = 0.00208 cu. ft.

Ml. of Effluent	Ml. of 0.04 N Sodium Hydroxide per 20 Ml. of Effluent	Grains per Gallon of Hydrochloric Acid, as Calcium Carbonate, in Effluent
100	0.05	0.29
200	0.05	0.29
300	0.05	0.29
400	0.05	0.29
500	0.05	0.29
600	0.05	0.29
700	0.05	0.29
800	0.05	0.29
900	0.10	0.58
1000	0.10	0.58
1100	0.30	1.76
1200	0.75	4.38
1300	1.10	6.43
1400	1.60	9.35
1500	2.20	12.88

Acid feed solution required 4.7 ml. of 0.04 N sodium hydroxide. This represented an initial hydrochloric acid concentration of 27.5 grains per gallon, as calcium carbonate.

solution was only slightly colored. The fact that no exchange properties were noted probably indicates that the amine group of the aniline had combined with the chlorine atom of the chlorinated Meadol. Thus the property of the amine group to add acid molecules was lost.

6. Discussion

In view of the fact that the aminated Meadol anionic exchange product was found to have poor resistance to alkaline regenerating solutions, it is believed that this material does not show promise of becoming of commercial importance. In addition, the exchange capacity of 3840 grains per cubic foot is low when compared to that of Amberlite IR-4, as shown in Tables 7 and 8, for which capacities in the vicinity of 20,000 grains per cubic foot are reported. It is of interest, however, to note that an aminated lignin product had been prepared. So far as is known, this is the first time that such a substance had been produced in which amine groups were attached to the lignin molecule in an apparently stable configuration.

V. VANILLIN

The fact that certain plants synthesize vanillin has been common knowledge for many years. The best example of such a plant is the vanilla bean, from which vanilla extract is obtained by alcoholic solution of the vanillin and other materials present in the dried bean.

The vanilla bean as a source of vanillin is handicapped by three important factors: (1) the vanilla bean can be grown only in a tropic climate, (2) its production requires a large amount of close attention, and (3) the plant is of the orchid family and must obtain its sustenance from the air. Because of the inaccessibility of the pollen to the ordinary insect, it is necessary that the flowers of the vanilla bean be hand pollinated when grown in certain localities where appropriate insects are lacking.

As a result of the high price for vanillin from the vanilla bean -- $10 to $15 per pound for the dried bean during normal times -- synthetic processes were developed for obtaining the active component. Natural and synthetic vanillin have now stabilized at some considerable price differential, largely because the select food trade still demands the natural vanilla. Synthetic vanillin finds its largest outlet in confections, bakery products, ice cream and in a surprisingly large number of perfume formulas. A considerable quantity is also used to render goods more attractive, more often to cover or mask a disagreeable odor inherent in the goods. Examples are in leather and rubber products manufacture.

Within recent years a new source of synthetic vanillin has developed. Lignin, in particular calcium lignosulfonate in sulfite waste liquors, may be processed to yield vanillin. Today over one third of the vanillin produced in the United States is made from lignin (7).

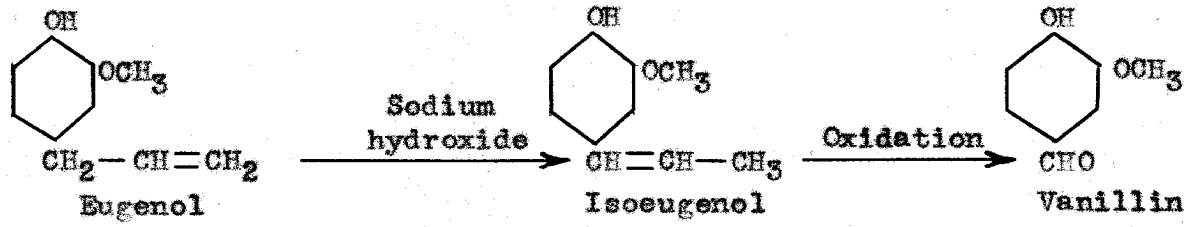
A. Synthetic Vanillin

The most important commercial sources of synthetic vanillin have been those involving the conversion of closely related naturally occurring products. Such a material is eugenol, found in oil of cloves. Another similar material is guaiacol, a substance found in small quantities in the tar resulting from the destructive distillation of beech wood. The synthesis of vanillin, however, is not limited to materials only obtainable from plant materials. Instead, benzene from coal tar serves equally well as a basic starting material.

Eugenol offers the advantage of requiring only a few steps for its transformation into vanillin, but the disadvantage of being relatively expensive. Benzene, on the other hand, offers the advantage of a cheap starting material, but the disadvantage of a large number of intermediate steps, some of which give rather low yields of the desired products. The net result is that vanillin from both sources is still a rather costly material, despite the fact that large quantities are used by the food and perfume industries.

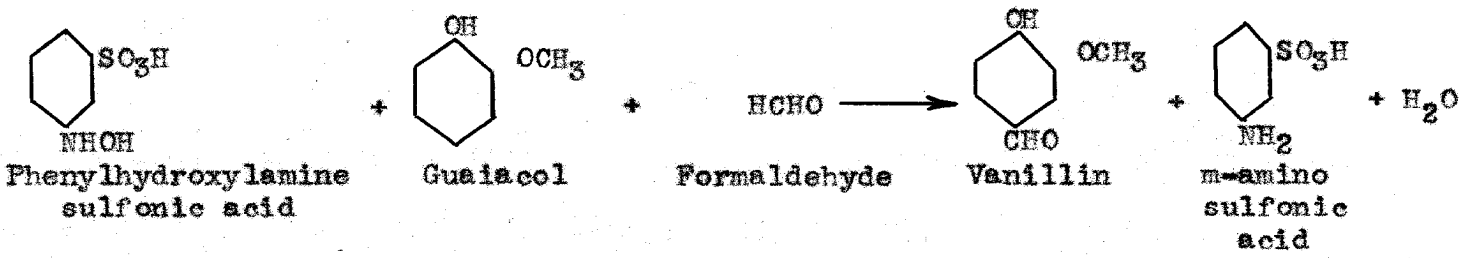
One of the earliest processes, and still one of the most common, for producing vanillin involves the conversion of eugenol into isoeugenol and

then into vanillin. The following reactions illustrate the essential steps:



In this case, the methoxyl group found in the vanillin was present in the original eugenol. When using strong oxidizing agents it is necessary to protect the hydroxyl group because of the relatively slight difference in oxidation susceptibility of the hydroxyl and propylene side chain. This is usually done with acetic anhydride. Strong oxidizing agents, such as dichromates and permanganates, are further objectionable because they tend to oxidize past the aldehyde stage to the acid, in which case vanillic acid is formed. Nitrobenzene, a much milder oxidizing agent, has been introduced recently and has proved to be very successful in not oxidizing beyond the desired aldehyde group to the undesired carboxyl group.

A considerable amount of work has been done on the synthesis of vanillin from cheap basic organic materials. Most important of the processes competing with eugenol is that starting with guaiacol. As mentioned earlier, guaiacol may be obtained as a product of the destructive distillation of beech wood or it may be synthesized from benzene. Phenol may be obtained from benzene by either of the standard methods, namely, chlorination followed by treatment with aqueous sodium hydroxide, or sulfonation followed by caustic fusion. Phenol is again carried through a similar treatment to obtain pyrocatechol. One hydroxyl group of pyrocatechol is then methylated with dimethyl sulfate to yield guaiacol. Once guaiacol is obtained, it is reacted



Phenylhydroxylamine sulfonic acid + Guaiacol + Formaldehyde → Vanillin + m-amino sulfonic acid + H_2O

with phenylhydroxylaminesulfonic acid and formaldehyde to yield vanillin as is shown in the above equation. Several modifications of the above synthesis exist, one of which involves the production of pyrocatechuic aldehyde by the above reaction from catechol after which the pyrocatechuic aldehyde is methylated with dimethyl sulfate. These reactions constitute the principal synthetic methods of obtaining vanillin.

B. Vanillin from Lignin

1. Laboratory methods

Kurschner (95) in 1928 is generally credited with being the first to report that vanillin, in fair yields, could be obtained from the lignin in waste sulfite liquors. This discovery is apparently the result of work carried out somewhat earlier (94) in which materials, such as pine shavings, pine mold, sulfite liquors, lignite, coal, and lignin, were subjected to sublimation conditions at extremely low pressures. In every case crystals of vanillic acid were obtained. At times this principal product was found mixed with vanillin and ammonium chloride. Kurschner suggested that the vanillic acid formed resulted from the oxidation of vanillin.

The original method used by Kurschner (95) for producing vanillin consisted in boiling waste sulfite liquors with a sodium hydroxide solution

under reflux while a stream of air was passed through the alkaline solution. The solution was acidified and extracted with various organic solvents, such as ether and benzene. The vanillin content was determined by sublimation and weighing or by colorimetric methods. The colorimetric methods used were the phloroglucinol-hydrochloric acid test and the orcinol-sulfuric acid test. Yields of between 10 to 21 per cent vanillin, based on lignin, were reported. The colorimetric methods used for determining the yield of vanillin were later found to give high results. In a subsequent paper (97) Kurschner and Schramek modified the procedure somewhat by extracting with trichloroethylene and precipitating the vanillin and other aldehydes with m-nitrobenzoylhydrazide.

In a later paper Kurschner and co-workers (98) stated that sodium sulfate and lime could be substituted for sodium hydroxide. Shortly afterward sodium carbonate and lime were reported (96) to be more economical than the sodium sulfate and lime treatment.

Honig and Ruziczka (81) investigated the conditions for obtaining a maximum yield of vanillin and found that the yield was greatly decreased by passage of air through the alkaline cook liquors because of oxidation. They reported that a maximum yield of vanillin was obtained from waste sulfite liquors by heating with sodium hydroxide in an autoclave for 3 hours at 160-170° C. and 5-6 atmospheres pressure. Vanillin was determined by precipitation with m-nitrobenzoylhydrazide.

Shoruigan and Smolyaninova (136) in a study of the various methods for determining vanillin from lignin concluded that it is difficult to isolate vanillin in the crystalline form, but that of the chemical methods available, precipitation with m-nitrobenzoylhydrazide was superior to other methods,

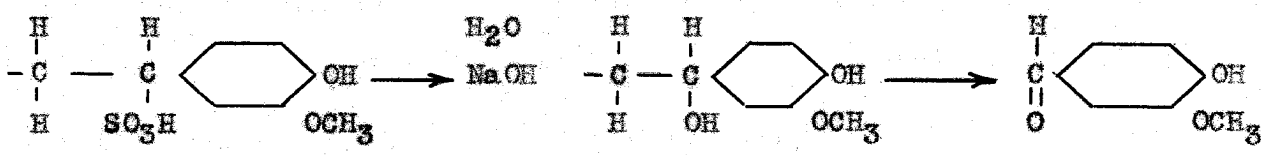
e.g., sodium bisulfite and hydroxylamine. Sulfite liquors were found to be more suitable than either sawdust of isolated lignin, because of the low yields obtained from these latter sources.

The preceding methods all involved an alkaline treatment of the lignin containing material. Pauly and co-workers (114) reported that vanillin could be obtained from lignin and lignin-containing materials by use of a "chromic acid acetic acid oxidation technique," in yields of as high as 8 per cent, based on the lignin, or 1.9 per cent, based on dry spruce wood. Shoruigan and Smolyaninova (136) used the same technique as given by Pauly, but were able to obtain a yield of only 0.16 per cent, based on the dry wood.

Hibbert and Tomlinson (143) further confirmed the fact that vanillin could be obtained from waste sulfite liquors. Yields of as high as 7 per cent of vanillin, based on the lignin content, were obtained. Prolonged boiling of the alkaline liquor was found to cause a slight decrease in the vanillin yield. Trichloroethylene was used to extract the acidified cook liquor. The aldehyde fraction was removed from this solvent by extraction with aqueous sodium bisulfite. The sodium bisulfite and vanillin addition compound was decomposed by the addition of acid and the vanillin was then precipitated as the m-nitrobenzoylhydrazide.

The exact mechanism by which vanillin is formed from lignin is not known, but for several years it was believed that only lignosulfonic acids gave vanillin on alkaline hydrolysis, since wood meal and isolated lignins yielded only negligible amounts of vanillin when treated in this manner. Hibbert and Tomlinson (144) concluded that the presence of the sulfonic acid group was necessary and that vanillin formation occurred as a two-stage

reaction, a preliminary hydrolysis of the sulfonic acid radical followed by an intramolecular fission. The following reactions illustrate the steps believed to take place:



Alvfeldt and Hagglund (6) found that the amount of vanillin formed from lignosulfonic acids, using the alkaline hydrolysis treatment, increased with the amount of sulfur present originally in the lignosulfonic acids.

In the preceding papers it was not recognized that syringaldehyde, a co-product, was precipitated with the vanillin. The reported yields of vanillin are therefore high. Considerable difficulty has been encountered in separating the two aldehydes quantitatively. Two methods are available. The first method developed involved the precipitation of the syringyl ammonium salt with anhydrous ethanol-ammonia (71). While approximately 90 per cent of the syringaldehyde as the ammonium salt could be recovered, only 50 per cent of the vanillin could be recovered from the filtrate. The second method involved a sublimation technique and is reported to give a satisfactory separation of the two aldehydes (71).

Freudenberg and co-workers (48) in 1940 disproved the contention that only lignosulfonic acids yield vanillin upon alkaline hydrolysis. The addition of a mild oxidizing agent, nitrobenzene, to the alkaline liquors made it possible to produce vanillin from wood meal and isolated lignins. Approximately 25 per cent of vanillin and syringaldehyde, based on lignin, were obtained from spruce wood. A repetition of the alkaline nitrobenzene treatment on

the lignin residue yielded additional vanillin derivatives to the extent of approximately 50 per cent.

The results of Freudenberg regarding the high yields of vanillin and related products obtained by the alkaline nitrobenzene treatment have been confirmed by Hibbert and co-workers (71)(27). A yield of vanillin and syringaldehyde in varying ratios was obtained from different plants, the sum of the two aldehydes ranging between 21 to 45 per cent, based on the lignin present. For woody materials (aspen, maple, sassafras) a yield of 40 to 45 per cent mixed aldehydes in a ratio of vanillin to syringaldehyde of 1 : 3 was obtained. With rye straw, corncobs and bamboo the yield of mixed aldehydes was 21 to 31 per cent and the ratio of the two aldehydes was about 1 : 1.

2. Commercial production

The high price of vanillin has made it economically feasible for the lignin in waste sulfite liquors to be utilized as a basic raw material. Commercial production of vanillin from this source has been characterized by rather low yields, only 2 to 5 per cent, and a considerable number of separational and purification steps, while the other synthetic methods have the advantage of high yields, 80 per cent or more, and only a few steps (62). Nevertheless, despite these manufacturing disadvantages, the fact that lignin is available at a price so much lower than that of either eugenol or guaiacol has led to an increasingly larger percentage of the vanillin produced in this country coming from lignin.

Current price quotations find synthetic vanillin from eugenol listed at $2.60 per pound, while vanillin from guaiacol and lignin are listed at a somewhat lower figure of $2.35 per pound.

The first patent application for producing vanillin by treatment of lignin containing materials was made by Sandborn, Salvesen and Howard (130) in 1933. The patent was assigned to the Marathon Paper Mills Company of Rothschild, Wisconsin. The patent claims state that any ligno-cellulosic material may serve as a raw material, but a concentrated source of lignin is desirable, such as the basic calcium lignosulfonate precipitated from waste sulfite liquors by the addition of lime. The basic calcium lignosulfonate is first treated with sodium sulfate to convert the calcium lignosulfonate to the sodium lignosulfonate. Calcium sulfate is precipitated and then removed by filtration. Sodium hydroxide is added to the soluble sodium lignosulfonate and the alkaline solution is heated under a pressure of between 130 to 200 pounds per square inch for a time of 1/2 to 1 1/2 hours in either a continuous flow cooking apparatus or in separate charges in a pressure vessel. Pressures above 200 pounds per square inch are reported to give a lower yield of vanillin, while a time of cook in excess of 1 1/2 hours tends to decrease the yield of vanillin even though the total yield of phenolic substances is increased. The alkaline cook liquors are then discharged and are acidified by the addition of sulfur dioxide. A lignin precipitate forms which is removed by filtration, while the sodium bisulfite vanillin addition compound remains in solution. The vanillin complex is broken down by the addition of sulfuric acid and the resultant solution is extracted with benzene to dissolve the vanillin and other phenolic materials. The benzene solution is then passed countercurrent to a sodium hydroxide solution through a series of scrubbing units. The sodium hydroxide solution from the first unit contains vanillin relatively free from other materials,

92 per cent vanillin, and the fraction from the second unit contains vanillin and non-aldehyde phenolic materials. The sodium hydroxide solution from the first extraction unit, rich in vanillin, is then treated with sulfuric acid and the vanillin is precipitated. The vanillin is further purified by recrystallization and sublimation. The alkaline solution containing the mixed vanillin and non-aldehyde materials is treated with sulfur dioxide to form the vanillin bisulfite complex which remains dissolved in the aqueous layer, while the non-aldehyde materials are then dissolved in benzene from which they are recovered later by evaporation or steam distillation of the benzene. Guaiacol is the principal material present in the non-aldehyde phenolic fraction. The vanillin bisulfite complex is decomposed by the addition of sulfuric acid and the vanillin which precipitates is purified in the same manner as mentioned previously.

Shortly afterward, in 1934, Tomlinson and Hibbert (74) made application for a patent for producing vanillin on a commercial scale by processing the waste sulfite liquors directly. A plant using this process is now operated in Canada by the Howard Smith Chemicals Limited of Montreal. The process is very similar chemically to that used by Hibbert and Tomlinson (143) for the determination of vanillin. The sulfite liquors are first concentrated by evaporation and then either boiled at atmospheric pressure or heated between 125° to 160° C. in a pressure vessel with an excess of sodium hydroxide. The vanillin, which is thus obtained in the form of its alkaline salt, is liberated by treatment of the alkaline cook liquor with an excess of carbon dioxide. The vanillin is extracted with an organic solvent, such as benzene or ethylene chloride. The organic solvent containing the vanillin is then

steam distilled and the vanillin residue is crystallized and sublimed for purification. The mother liquor, from which the vanillin has been extracted, is filtered to remove insoluble calcium salts as calcium sulfate and calcium sulfite. The filtrate, containing the waste alkali principally in the form of the alkali bicarbonate, is then dried and incinerated to recover sodium carbonate which is recausticized for re-use in the process.

Hatch (68) devised a continuous reactor for heating sulfite waste liquors with sodium hydroxide. The sulfite liquor is adjusted to a pH of 13 and is then passed through the reactor. A temperature of approximately 200° C. and a pressure of 215 pounds per square inch is maintained. The cook liquors pass through the reactor in approximately 15 minutes after which they are cooled immediately in order to stop any decomposition of the vanillin. Patent rights to the equipment have been assigned to the Weyerhaeuser Timber Company of Tacoma, Washington.

The preceding processes all require neutralization of the alkaline cook liquors, since extraction of the vanillin must be carried out in a slightly acid solution. Not only is acid required for the neutralization, but the unreacted lignosulfonic acid is precipitated and the presence of the precipitate renders the extraction of the acidified solution difficult. The precipitate causes emulsion formation, absorbs a large amount of the organic solvent used and occludes a considerable amount of vanillin.

From the preceding paragraph it is apparent that a much more satisfactory removal of vanillin could be obtained if vanillin could be extracted from the alkaline solution. In a modification of his previous patent, assigned to the Marathon Paper Mills Company, Sandborn (131) pointed out that it was

possible to extract sodium vanillate from the alkaline cook liquors directly with butyl alcohol. The resulting butyl alcohol solution containing vanillin is steam distilled and the aqueous solution of sodium vanillate is acidified with sulfur dioxide to yield the soluble vanillin bisulfite addition product. Most of the non-aldehyde phenolic materials separate out as a tarry mass in this step. The vanillin bisulfite complex is decomposed with sulfuric acid and the crude vanillin then separates out. Purification is brought about by recrystallization and sublimation.

Williams and Rafanova (156) were granted a Russian patent in which it was claimed that when sulfite waste liquors are acidified and the clear solution obtained after separation of the insoluble lignosulfonic acid is extracted with an organic solvent vanillin is obtained.

A Swiss patent (78) was granted in 1940 in which it was claimed that the conversion of the calcium lignosulfonate in waste sulfite liquors to sodium lignosulfonate by treatment with sodium sulfate or sodium carbonate resulted in an increase in the yield of vanillin of over 50 per cent when digested with sodium hydroxide. This method is similar to that used by the Marathon Paper Mills Company (130) of this country.

The commercial methods for the production of vanillin from lignin containing materials are, for the most part, closely related and all, with the exception of the Russian patent to Williams and Rafanova (156), depend upon an initial treatment with sodium hydroxide for the formation of vanillin. Vanillin production from the lignin in waste sulfite liquors appears to be well established and there is evidence to support the view that an increasingly larger proportion of the vanillin produced in this country will be obtained from this source.

VI. EXPERIMENTAL-VANILLIN FROM FURFURAL OAT HULL RESIDUE

Substances containing a high percentage of lignin are desirable as raw materials for the production of vanillin on a commercial scale, otherwise a large amount of inert material must be handled. The furfural oat hull residue is such a material.

The recent discovery by Freudenberg and co-workers (48) of the alkaline nitrobenzene treatment has shown that it is possible to obtain high yields of vanillin and closely related materials from all types of lignin and lignin containing materials. Until the development of this method of treatment, lignin containing materials, other than the lignosulfonic acid salts obtained from waste sulfite liquors, yielded only negligible quantities of vanillin when digested with sodium hydroxide solutions.

Accordingly, the feasibility of using the furfural oat hull residue as a raw material for the production of vanillin was investigated. The alkaline nitrobenzene treatment discovered by Freudenberg (48) and modified by Hibbert (71) has been used as the basic method of treatment for determining the amount of vanillin formed.

A. Experimental Procedure

The essential steps used for obtaining vanillin from the furfural oat hull residue are shown in flow sheet form in Figure 10.

The initial step involving the treatment of the furfural oat hull residue with sodium hydroxide and nitrobenzene was carried out in a 5 liter vertical

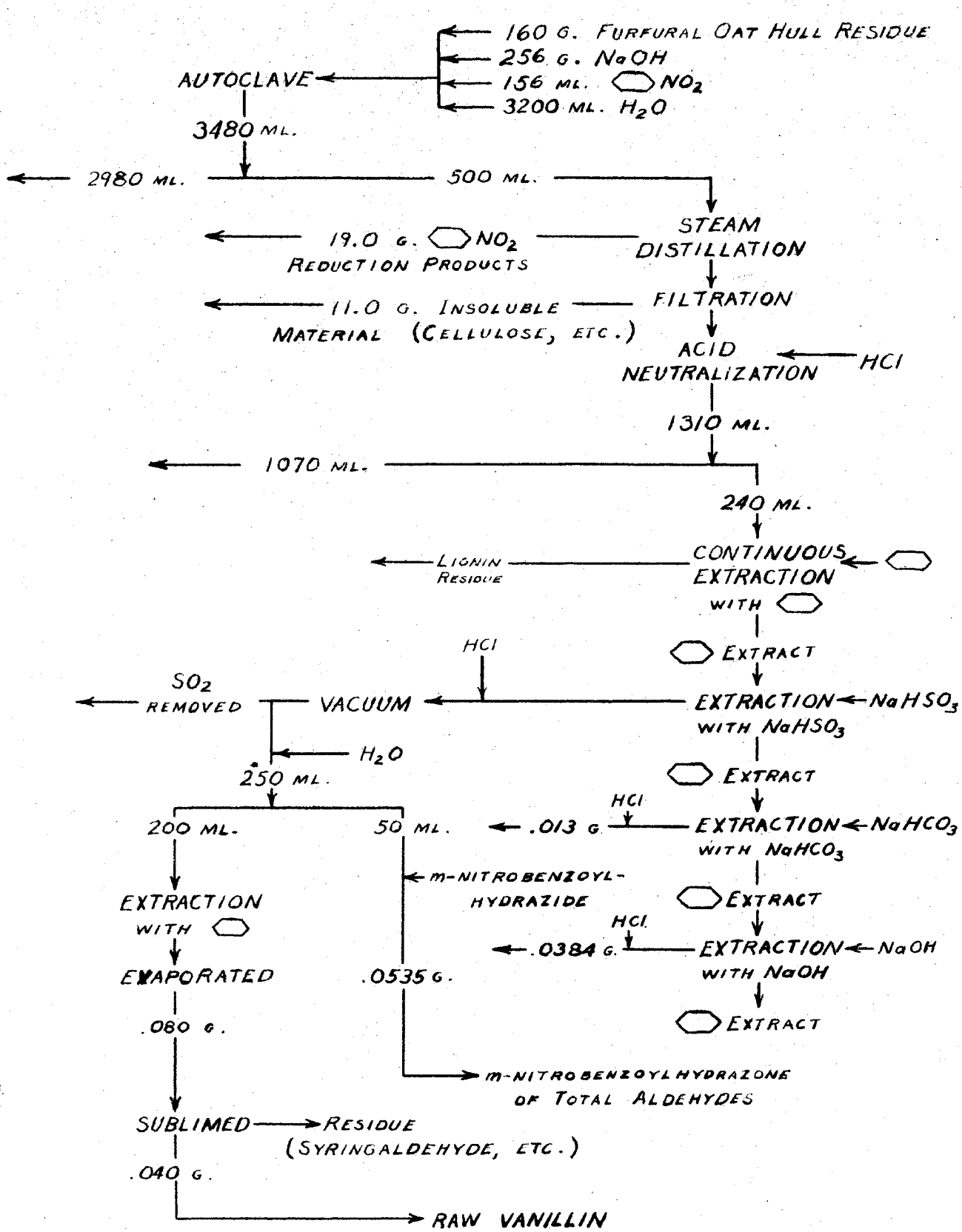


FIG. 10. VANILLIN FROM FURFURAL OAT HULL RESIDUE

type hand-stirred high pressure steel autoclave. One hundred and sixty grams of the furfural oat hull residue, 6 per cent moisture, was stirred into a solution containing 256 grams of sodium hydroxide dissolved in 3200 milliliters of distilled water. To this was added 156 milliliters of nitrobenzene. The autoclave was heated to between 160° to 165° C. and was held within this temperature range for a period of 3 hours, during which time the mixture was stirred rapidly. Following this, the autoclave was allowed to cool overnight previous to removing the contents. The nitrobenzene reduction products deposited on the bottom of the container. Very little nitrobenzene apparently was left unreacted, since only a faint odor of nitrobenzene could be detected. After discharging and rinsing the volume of the reaction mixture was 3480 milliliters.

A charge of 500 milliliters was steam distilled in order to remove the nitrobenzene reduction products, largely azoxybenzene and azobenzene. The steam distillation was carried out in a large 5 liter round bottom flask. A flask of this size was necessary because considerable difficulty had been encountered due to the tendency of the cook liquors to foam. Usually 36 hours of steam distilling was necessary before a clear distillate was obtained. The first portion distilled contained the major portion of what nitrobenzene was left unreacted since its characteristic odor could not be detected in later fractions. After several hundred milliliters of water, nitrobenzene and its reduction products had been obtained, it was noted that definite reddish brown crystals of azobenzene were formed when the reddish oily material was separated and cooled. Recrystallization from ligroin gave a material which melted at 67-68° C. The melting point of azobenzene is 68° C.

The total volume of the alkaline liquors at the conclusion of the steam distillation was 1260 milliliters.

The solution was then filtered in a Buchner filter and the cellulose residue was washed twice with 5 per cent sodium hydroxide and then with distilled water. Filtration was slow and difficult. Following this the filtrate was acidified with concentrated hydrochloric acid to a pH of 3, as indicated by a Congo Red test paper. The lignin material was precipitated. The fragrant odor of vanillin was readily discernible. At the conclusion of the neutralization the total volume was 1310 milliliters.

The next step involving the extraction of the vanillin was the most difficult of the entire procedure. Considerable difficulty was encountered with emulsion formation and the resulting separational problems. During the course of the investigation several extractors were devised. The type shown in Figure 11 has proved to be the most satisfactory. The use of interchangeable ground glass equipment made it possible to dismantle the equipment readily if difficulties in operation arose. Likewise, the equipment was readily reassembled for use. The previous types of extractors used corks and rubber stoppers. The corks tended to leak, while the rubber stoppers swelled and were slightly dissolved by the benzene solvent. With both corks and rubber stoppers, it was difficult to dismantle and reassemble the equipment. The interchangeable ground glass equipment was satisfactory in every respect.

Benzene was used as a solvent. The extraction apparatus was operated continuously for 72 hours. Occasionally the insoluble lignin which tended to settle to the bottom of the extraction tube was stirred. Operation at a

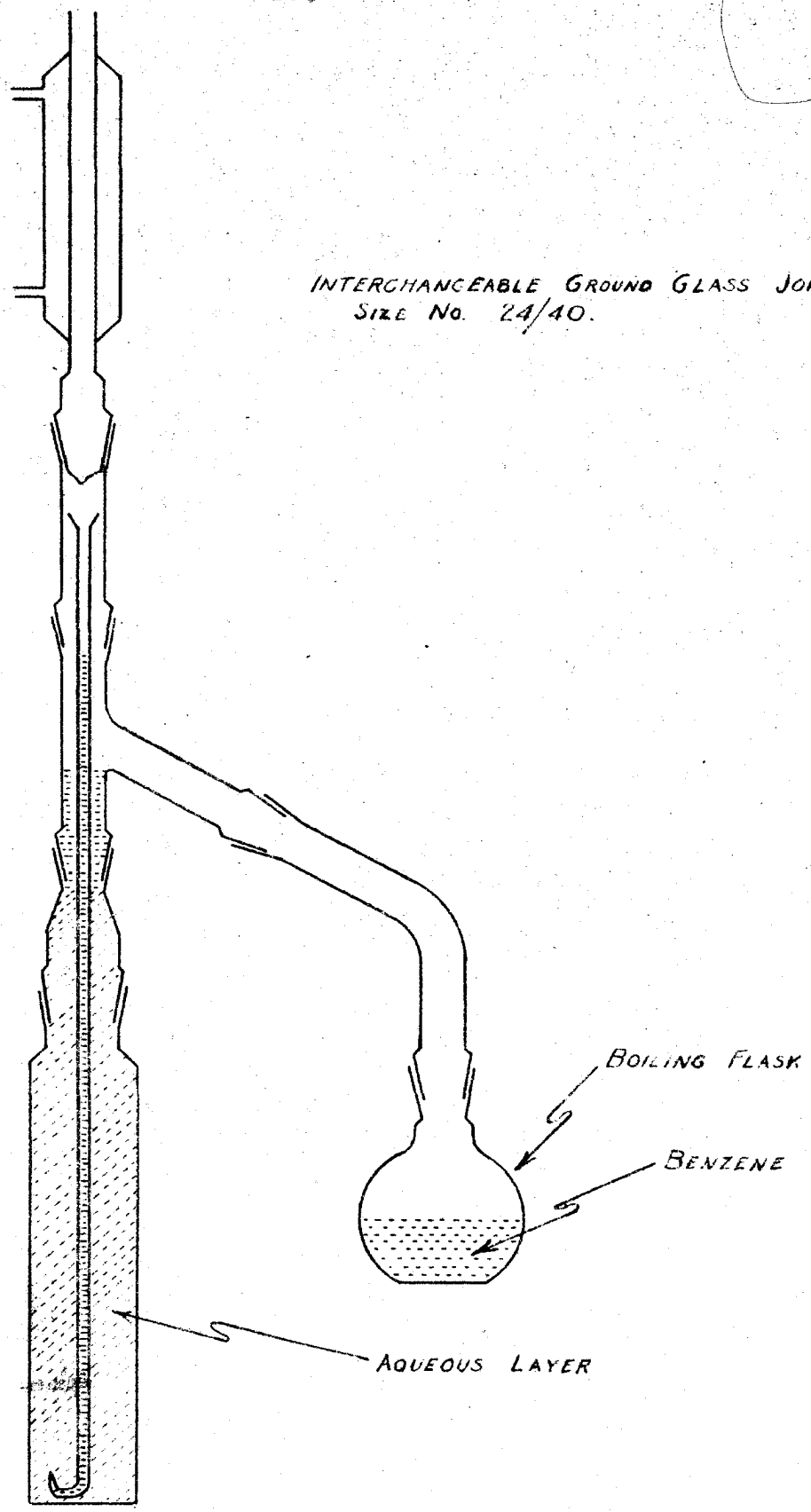


FIG. 11. CONTINUOUS EXTRACTOR

fairly rapid rate tended to provide a mixing action and thus kept the major portion of the lignin and any occluded or adsorbed vanillin in suspension. The first portion of the solvent discharged was colored yellow orange, but after some time a colorless liquid was obtained. The extraction tube held approximately 240 milliliters of solution. Approximately 5 centimeters of space was left above the aqueous layer as a calming space, so that any emulsion formed would not be carried over into the boiling flask.

Following the continuous extraction step the benzene extract was shaken successively in a separatory funnel with solutions of 20 per cent sodium bisulfite, 8 per cent sodium bicarbonate and 5 per cent sodium hydroxide. Ten extractions of 15 milliliters each were made with the various solutions. The sodium bicarbonate and sodium hydroxide extracts were colored reddish brown for the first few extracts, but cleared up shortly thereafter.

The aqueous bisulfite extract was acidified slightly with concentrated hydrochloric acid. The acidified solution was placed in a 250 milliliter Erlenmeyer flask and the sulfur dioxide was removed under reduced pressure at room temperature. The liquid was then transferred to a volumetric flask and was diluted to 250 milliliters.

The total aldehydes in 50 milliliters of the above solution were determined by precipitation as the m-nitrobenzoylhydrazone. Fifteen grams of sodium acetate were added as a buffer, after which the solution was heated to 60° C. To this was added 25 milliliters of a saturated aqueous solution containing approximately 0.3 gram of m-nitrobenzoylhydrazide. A light brown precipitate formed after a short time. The solution was heated on a water bath for 1/2 hour and then allowed to stand overnight. The precipitate was

filtered on a weighed Pyrex crucible with a sintered glass bottom, was washed with distilled water and then dried at 95° C. The yield of aldehydes was calculated as vanillin from the m-nitrobenzoylhydrazone. Previously, before the presence of syringaldehyde in this fraction had been discovered, it had been believed by many investigators that this entire fraction was made up of vanillin. The weight of the m-nitrobenzoylhydrazone was 0.0535 gram, or 10.5 per cent of aldehydes, based on 30.2 per cent Klason lignin in the furfural oat hull residue; or 3.2 per cent based on the furfural oat hull residue itself. Although the furfural oat hull residue analyzed 40.0 per cent Klason lignin, actually only 30.2 per cent lignin was present since it was found that the ash present in the lignin residue amounted to 9.8 per cent of the original furfural residue on the dry basis.

The total bisulfite-soluble materials were isolated by extraction of the remaining solution with benzene. Ten extractions of 15 milliliters each were made. The benzene extract was then evaporated under a vacuum in a 150 milliliter wide mouth flask on a water bath. A yellow oily fraction with white crystals dispersed throughout was obtained. The material had the very pleasant odor of vanillin when smelled at some distance, but when held close to the nose a slightly disagreeable oily odor was detected. After standing for several days the disagreeable odor decreased considerably. A yield of 0.080 gram of residue or 8.4 per cent, based on lignin, was obtained. The fact that this value is lower than that obtained by precipitation with m-nitrobenzoylhydrazide is probably due to loss of vanillin and related materials during extraction and while the benzene was being vaporized.

The recovered bisulfite-soluble fraction was placed in a small size

sublimation tube, fitted with a cold finger, and was heated at 60° C. at an absolute pressure of 10 millimeters. It was impossible to obtain the low pressure of 1.5 millimeters, used in the Hibbert sublimation technique (71) for the separation of vanillin and syringaldehyde, with the equipment available. A white cloud formed on the cold thimble within a short time. After approximately 3 hours no more material sublimed. From time to time the crystals were scraped off of the cold thimble for weighing. A very slight amount of faintly yellowish material was carried over during the latter stages. The weight of the raw vanillin was 0.04 gram or 4.2 per cent, based on lignin. The melting point of the crystals was found to be 68-75° C. The melting point of pure vanillin is 80-81° C.

A portion of the raw vanillin was recrystallized from ligroin. The resulting crystalline product melted at 79-81° C. The melting point of pure vanillin is 80-81° C. Another portion of the recrystallized vanillin was reacted with phenylhydrazine to form the phenylhydrazone of vanillin. A small amount of vanillin was dissolved in 5 milliliters of 50 per cent ethyl alcohol. Approximately 1/2 milliliter of a saturated sodium bisulfite solution was added to prevent the formation of any tarry products. To the clear solution 1/2 milliliter of phenylhydrazine and about one drop of acetic acid were added. After warming for a few minutes the mixture was cooled. Within a short time crystals appeared. These were filtered, dried and the melting point taken. The phenylhydrazone of the vanillin product melted at 103-104° C. The melting point of the phenylhydrazone of pure vanillin is 105° C. The substance is therefore vanillin.

The yellowish oily residue remaining in the bottom of the sublimation

tube was not investigated further. It was not possible to duplicate the separational method of Hibbert (71) for obtaining syringaldehyde from the oil, because of inability to reach the vacuum required, 1.5 millimeters, with the apparatus used.

The sodium bicarbonate fraction was neutralized with hydrochloric acid to Congo Red test paper, pH of 3. A brownish precipitate formed. After standing overnight, the precipitate was filtered in a weighed Pyrex crucible with a sintered glass bottom, was dried and then weighed. A weight of 0.013 gram, or 1.1 per cent, based on lignin, was obtained. In previous runs the acidified solution had been extracted in a separatory funnel with benzene. Evaporation of the benzene gave approximately the same yields as by the preceding method. Because of an insufficient quantity of material, the separation and identification of the various components making up this carboxylic acid fraction were not carried out, but it is believed that syringic and vanillic acids were the principal materials present.

The sodium hydroxide fraction was neutralized with hydrochloric acid to a pH of 3 using Congo Red test paper. A yellowish orange precipitate formed. The precipitate was filtered in a weighed Pyrex crucible with a sintered glass bottom and was washed with a small amount of water. After drying at 95° C. the crucible and contents were weighed. A yield of 0.0384 gram, or 3.2 per cent, based on lignin, was obtained. The various materials making up this phenolic fraction were not identified. Freudenberg (48) indicates that guaiacol was one of the principal materials present.

B. Discussion of Results

Vanillin may be obtained from the furfural oat hull residue by the action of sodium hydroxide and nitrobenzene. Table 22 summarizes the results obtained on the basis of both the lignin content and the furfural oat hull residue itself.

Table 22

Oxidative Alkaline Cleavage of the Furfural Oat Hull Residue

	Per Cent Yield Based On	
	Lignin	Furfural Oat Hull Residue
Total aldehydes as (m-nitrobenzoylhydrazone)	10.5	3.2
Isolated aldehydes	8.4	2.5
Raw vanillin	4.2	1.3
Sodium bicarbonate soluble fraction	1.1	0.3
Sodium hydroxide soluble fraction	3.2	1.0

The yield of total aldehydes, based on the lignin content, was 10.5 per cent. This is approximately 50 per cent of that reported for corncobs and rye straw by Hibbert (71). It is felt that higher yields would have been obtained in this work if a rotating type autoclave had been available so that better agitation and contact between the relatively insoluble nitrobenzene and the lignin dissolved in the aqueous alkaline solution

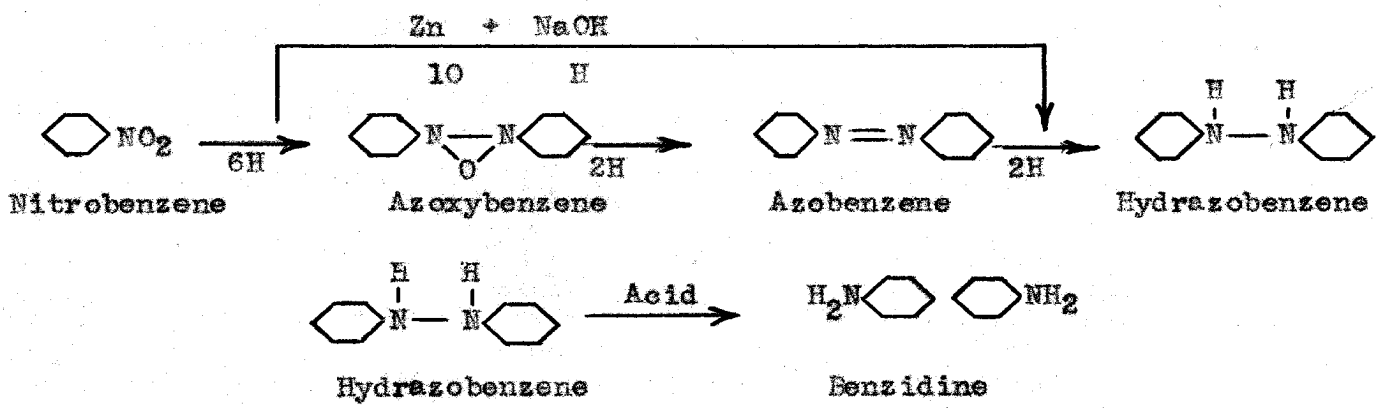
could have taken place. In Hibbert's work, such an autoclave was used.

Approximately 50 per cent of the aldehyde fraction was made up of vanillin. For corncobs, rye straw and bamboo, Hibbert (71) reported a ratio of vanillin to syringaldehyde of 1 : 1. Although syringaldehyde was not isolated in this investigation, it seems probable that a similar ratio holds for the furfural oat hull residue. For woody materials the ratio of vanillin to syringaldehyde was approximately 1 : 3.

The alkaline nitrobenzene method of treating lignin to obtain vanillin appears to offer definite advantages over the use of alkali alone, as is used at present with the lignosulfonic acids in waste sulfite liquors; in addition to making it possible to obtain vanillin from lignin containing materials which did not yield vanillin by this latter method of treatment. The increased yield of vanillin, approximately 2 to 3 times, would far more than offset the cost of the nitrobenzene and any additional processing. The same equipment could be used, with the one exception that an additional step would be required for the removal of the nitrobenzene reduction products. Either steam distillation or benzene extraction of the alkaline liquors directly following the alkaline nitrobenzene pressure cook would be satisfactory.

The nitrobenzene reduction products which are principally azoxybenzene, azobenzene and a small amount of aniline should nearly offset the cost of nitrobenzene. In themselves, they possess no great use, but they are the intermediate products in the production of hydrazobenzene which is converted to benzidine by passing through the benzidine rearrangement. A considerable demand exists for benzidine in the dye field, where it is used in the pro-

duction of the benzidine type dyes which are direct dyes for cotton. The following reactions show the various intermediate compounds involved in the conversion of nitrobenzene to benzidine:



The first step involving the conversion of nitrobenzene to azoxybenzene requires 6 atoms of hydrogen, while the remaining two steps between azoxybenzene and hydrazobenzene require only 4 atoms of hydrogen. Freudenberg (48) reported that azoxybenzene was the principal reduction product obtained, however, in this work azobenzene was the reduction product present in greatest amount. In the various runs conducted, it was noted that the degree of reduction varied considerably. This factor bears further investigation. In any event, regardless of whether azoxybenzene or azobenzene is the principal product, at least 60 per cent of the hydrogen necessary for the reduction could be provided by this process. In effect then, a considerable saving would be brought about by reducing the quantity of zinc necessary to produce hydrazobene from nitrobenzene by using the azoxybenzene and azobenzene mixture obtained as a by-product from this process. Current price quotations list benzidine and nitrobenzene at $0.70 and $0.07 per pound, respectively.

Added to these advantages are the larger amounts of materials obtained

in the sodium bicarbonate fraction, carboxylic acids, and in the sodium hydroxide fraction, phenolic materials. The latter fraction should offer promise for use in the plastics field.

VII. CONCLUSIONS

(1) Organic cationic exchange materials can be prepared from alkali lignin recovered from waste liquors of the soda pulping process upon treatment with strong sulfuric acid.

(2) Exchange materials of high capacity and satisfactory properties have been prepared from alkali type lignins. These materials compare favorably with exchange materials now being marketed.

(3) A cost estimate indicates that the exchange material prepared from Meadol can be produced at a price at least as cheap and probably cheaper than that of organic cationic exchange materials now being marketed.

(4) The process proposed for producing the cationic exchange material presents no great difficulties from a design, construction or corrosion standpoint.

(5) The exchange material can be regenerated with either salt of acid solutions.

(6) It is possible to produce exchange materials with a wide range of chemical and physical properties, thus making it possible to prepare materials for a particular purpose.

(7) The temperature of sulfonation has a considerable effect on the properties of the exchange material. A temperature of between 85° to 95° C. results in a material with a maximum volumetric exchange capacity. On the weight basis, the exchange capacity increases with increase in temperature. Gelling does not occur at temperatures below 85° C. The higher the temper-

ature of sulfonation the lower is the density and the less is the tendency to impart color to the water being softened.

(8) Exchange materials prepared with larger amounts of sulfuric acid per unit weight of lignin have higher capacities than those prepared with lesser amounts of sulfuric acid per unit weight of lignin.

(9) Higher concentration sulfonating acids tend to give materials with slightly higher exchange capacities, as well as giving substances with less of a tendency to impart color to the water being softened.

(10) A maximum amount of sulfur is introduced into the sulfonated alkali lignin at some temperature between 80° to 100° C. At temperatures lower and higher than this critical temperature the amount of sulfur introduced decreases. Higher concentration sulfonating acids introduce a higher percentage of sulfur into the sulfonated lignin. Increasingly larger amounts of sulfonating acid of the same concentration per unit weight of lignin introduce a larger amount of sulfur.

(11) The quantity of sulfur present, if as sulfonic acid, is insufficient to account for the total observed exchange capacity. This is probably due to oxidation of the lignin to produce additional carboxyl, phenol and other groups capable of exchange properties.

(12) An exchange material of very high exchange capacity can be prepared from acid precipitated soda lignin recovered from cornstalk cook liquors upon sulfonation.

(13) Cationic exchange materials may be produced from the furfural oat hull residue itself, or from the Klason lignin obtained from this source, upon sulfonation. The exchange capacity is very high on the weight basis,

but the low density and tendency to "throw" color are disadvantages of exchange materials prepared from this raw material.

(14) An anionic exchange material can be prepared from alkali lignin by first chlorinating and then aminating.

(15) The aminated Meadol anionic exchange material, while effective in adsorbing acid, was found to have a low capacity and poor resistance to alkaline regenerating solutions.

(16) Vanillin can be obtained from the furfural oat hull residue by the alkaline nitrobenzene treatment.

(17) The use of the alkaline nitrobenzene treatment offers economic advantages over the use of alkali alone for obtaining vanillin from lignin containing materials.

VIII. SUMMARY

At the present time the quantity of lignin utilized commercially represents only a minute fraction of the total amount produced each year. Accordingly, various ways in which larger amounts of lignin or lignin containing materials could be utilized were studied.

The utilization of lignin was studied from the standpoint of preparing ionic exchange materials, both cationic and anionic, for use in the field of water treatment and the possibility of producing vanillin from the furfural oat hull residue by use of the alkaline nitrobenzene method of treatment. It was discovered that an excellent cationic exchange material could be prepared by the sulfonation of Meadol, an alkali type of lignin recovered from the waste liquors of the soda paper pulping process. A similar type of exchange material, with a very high exchange capacity, was prepared from cornstalk alkali lignin obtained by precipitation with acid from alkaline cornstalk cook liquors. Cationic exchange materials were also prepared from the furfural oat hull residue itself and a Klason type lignin obtained from this source. An aminated lignin material was prepared from Meadol which showed acid adsorbtive properties. Vanillin and related materials were obtained from the furfural oat hull residue when subjected to the alkaline nitrobenzene method of treatment.

The production of cationic exchange materials from alkali types of lignin by the proposed method shows considerable promise from the standpoint

of both quality and cost. The use of the alkaline nitrobenzene method of treatment of lignin or lignin containing materials for the production of vanillin and related material offers the advantages of high yields and valuable by-products.

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53. Fuchs, W. and Horn, O. Lignin Chemistry. X. Genuine lignin. Ber., 62B, 1691-3 (1929).
Studies on lignin indicate a formula weight of between 800 and 850 for the lignin building unit or a multiple thereof for the lignin molecule.

54. Fuchs, W. and Daur, R. New investigations regarding the constitution of the pine lignins, humic acids and humins. Brennstoff-Chem. 12, 266-8 (1931). Original not seen. Abstracted in C. A. 26, 470 (1932).
Formulas for lignin and humic acids are presented. Humic acids and lignin are closely related, except that the humic acids have been oxidized to yield a large number of hydroxyl and carboxyl groups.

55. Furness, R., Anderson, L. and J. Crossfield and Sons, Ltd. Ion-exchanging compounds. French Patent 833,113 (Oct. 12, 1938). Original not seen. Abstracted in C. A. 33, 3047 (1939).
Lignosulfonic acids are liberated from sulfite liquor by treating with a strong non-oxidizing acid. The lignosulfonic acids are polymerized by treatment with an acid or by heat treatment to form a water insoluble product. This product is hardened by dehydration to form a substance capable of being granulated. The mineral acid may be sulfuric and the quantity used may be sufficient to effect the liberation, polymerization and hardening in a single stage. The product may be used for a water softener.

56. Furness, R. and Crosfield and Sons, Ltd. Base-exchange materials. British Patent 455,374 (Oct. 14, 1936). Original not seen. Abstracted in C. A. 31, 2330 (1937).
A base-exchange material is obtained by treating granular coal with a sulfonating agent, e.g., H_2SO_4, oleum, or $ClHSO_3$, at about 95° C., and washing.

57. Furness, R. and Crosfield and Sons, Ltd. Imparting ionic-exchange capacity to coal. British Patent 486,471 (June 3, 1938). Original not seen. Abstracted in C. A. 32, 8652 (1938).
Dry granulated coal is subjected to the action of fuming H_2SO_4 or SO_3 dissolved in liquid SO_2 until the reaction product shows the desired ion-exchange capacity. The material is washed free from unreacted acid.

58. Gans, R. Artificial zeolite. British Patent 3,494 (Feb. 12, 1907). Original not seen. Abstracted in C. A. 2, 2605 (1908).
Artificial zeolites are made by melting an aluminate with an alkali silicate or with alkali and quartz in such a ratio that the alkali will just combine with the silica and the alumina.

59. Goetz, P. C. (to Permutit Co.). Removing acid and fluorine from water. U. S. Patent 2,139,227 (Dec. 6, 1938). Original not seen. Abstracted in C. A. 33, 2259 (1939).
For removing both acid and fluorine from water. Raw water is passed through a bed of granular hydrated metallic oxide such as hydrated ferric oxide in gel form. Regeneration of the bed is brought about by washing with a dilute alkaline solution, such as one of NH_3 and with a dilute acid solution, such as one of acetic acid containing sodium acetate.

60. Griessbach, R. and Eisele, J. Utilizing material rich in lignin. U. S. Patent 1,666,696 (April 17, 1928). Original not seen. Abstracted in C. A. 22, 2057 (1928).
Lignin from wood meal or similar materials is extracted with an organic halogen containing solvent, such as ethylene-chlorohydrin to extract vanillin and other substances which may be recovered.

61. Groggins, P. H. "Unit Processes in Organic Synthesis." Second Edition. McGraw-Hill Book Co., New York. (1938). p. 613.
The Scholler-Tornesch system of wood saccharification is described.

62. Groggins, P. H. "Unit Processes in Organic Synthesis." Second Edition. McGraw-Hill Book Co., New York. (1938). p. 377, 520.
Various commercial processes for producing vanillin are described.

63. Hägglund, E. and Urban, H. Lignin acetals. Cellulosechem. 8, 69-71 (1927).
Lignin from ground wood was extracted by the action of ethyl alcohol, butyl alcohol, amyl alcohol, and a hydrochloric acid catalyst.

64. Hägglund, E. and Urban, H. Lignin acetals. Cellulosechem. 9, 49-53 (1928).
An investigation of the reactive groups in lignin from various sources.

66. Harris, E. E. Utilization of waste lignin. Ind. Eng. Chem. 32, 1049-52 (1940).
Chemical research on the fundamental aspects of lignin from waste products is aiding in the solution of this problem. A knowledge of the various external groups--hydroxyl, methoxyl, and unsaturated--aids in foretelling the reactions of lignin. Hydrogenation of lignin suggests a way of converting lignin wastes into valuable products.

67. Harris, E. E., Sherrard, E. C. and Mitchell, R. L. Some reactions of maple and spruce lignin. J. Am. Chem. Soc. 56, 889-93 (1934).
The reactive groups in the lignin building unit have been classified. The hydroxyl groups are not free until after hydrolysis. Evidence indicates that isolated lignin exists in a keto form, while native lignin exists in the enolic form combined with carbohydrates.

68. Hatch, R. S. (to Weyehaeuser Timber Co.). Method of producing vanillin from waste sulfite liquor. U. S. Patent 2,099,014 (June 27, 1936).
A continuous process for obtaining vanillin from waste sulfite liquor is described.

69. Herzog, R. O. and Hillmer, A. Lignin. III. Ber. 64B, 1288-306 (1931).
Studies on the structure of lignin utilizing the ultra-violet absorption spectra method indicate a benzenoid structure for lignin. Various groups thought present are indicated.

70. Heuser, E. and Herman, F. Fusion of lignin, cellulose and wood with caustic potash. Cellulosechem. 5, 1-6 (1924).
Fusion of the various plant components was carried out. High yields of oxalic acid were obtained under oxidizing conditions. In the absence of air yield of catechol and protocatechuic acid as high as 25 per cent were obtained.

71. Hibbert, H., McCarthy, J. L. and Creighton, R. H. J. Studies on lignin and related compounds. LIX. Aromatic aldehydes from plant materials. J. Am. Chem. Soc. 63, 3049-52 (1941).
An oxidizing mixture of sodium hydroxide and nitrobenzene was used on many plant materials. Vanillin and syringaldehyde were obtained in varying ratios, the sum of the two varying from 21 to 48 per cent based on the lignin present.

72. Hibbert, H. and Marion, L. Nitration of glycol lignin. Can. J. Research 3, 130-0 (1930).
Glycol lignin was nitrated and the resulting products were studied.

73. Hibbert, H. and Rowley, H. J. Isolation of spruce wood lignin. Can. J. Research 2, 357-63 (1930).
Lignin from spruce wood was extracted with ethylene glycol.

74. Hibbert, H. and Tomlinson, G. H. Manufacture of vanillin from waste sulfite pulp liquor. U. S. Patent 2,069,185 (Dec. 27, 1934).
The entire waste sulfite pulp liquors are processed and the vanillin is recovered by extraction with benzene.

75. Hilpert, R. S. and Hellwage, H. Beech-wood lignin, a reaction product of carbohydrates in the lignin determination. Ber. 68B, 380-3. (1935).
The existence of lignin in the plant as such is denied. It is believed that lignin is a reversion product from the action of acids on certain methylated carbohydrates.

76. Hilpert, R. S. and Hellwage, H. The degradation of woods. Cellulosechem. 17, 25-8 (1936).
Lignin is probably not present as such in wood, but it is a secondary reaction product formed from carbohydrates.

77. Hissink, D. J. The relation between the ph value, the degree of saturation and the humus of some humus soils. Proc. 2nd Comm. Intern. Soc. Soil Sci., A. Groningen (Holland) 198-207 (1926). Original not seen. Abstracted in C. A. 20, 3056 (1926).
Results indicate that humic substances have a greater power of base adsorption than clays. Base-exchange was noted with lime and acid.

78. Hoffmann, F. - La Roche and Co. Akt.-Ges. Vanillin from sulfite cellulose liquor. Swiss Patent 210, 834 (Oct. 16, 1940). Original not seen. Abstracted in C. A. 35, 5700 (1941).
An increase in the yield of vanillin from waste sulfite liquor is secured if the Ca of the calcium lignosulfonate is removed by treatment with Na_2SO_4, Na_2CO_3 or other alkali salt. When the resulting material is heated with NaOH at 160-170° C. for three hours an increase of over 50 per cent in the vanillin yield is obtained.

79. Holmberg, B. Alcoholate digestion of wood. Svensk. Kem. Tids., 37, 189-97 (1925).
Evidence indicates that the lignin in wood occurs as an acetylated substance with carbohydrates, the latter as an alcohol and the lignin as a carbonyl component.

80. Holmes, E. L. Removal of acid from water. Canadian Patent 385,929 (Dec. 26, 1939). Original not seen. Abstracted in C. A. 34, 1787 (1940).
Acid containing water is passed through a granular bed of resin prepared by the reaction of a monosaccharide, a disaccharide or a substance that yields a monosaccharide or a disaccharide on hydrolysis, with m-phenylenediamine or 5-alkyl-m-phenylenediamine. The resin is regenerated by passing an alkaline solution through it.

81. Hönig, M. and Ruzeczka, W. Formation of vanillin from sulfite cellulose waste liquors and its gravimetric determination. Z. angew. Chem., 44, 845-7 (1931).
Boiling sulfite waste liquors with sodium hydroxide gives vanillin, which can be determined as the m-nitrobenzolyl-hydrazine. The yield of vanillin is greatly decreased by passage of air during boiling, because of oxidation, and is greatly increased by heating for 3 hours at 160-70° and 5-6 atmosphere.

82. Howard, G. C. A progress report on waste sulfite liquor. Ind. Eng. Chem. 22, 1184-5 (1930).
Waste sulfite liquor is treated with lime in a series of reaction vessels and settling tanks. The sludge in the first tank consists largely of calcium sulfite which is reused. Calcium lignosulfonate is precipitated in later tanks upon addition of more lime. This is filtered and dried. The effluent liquors now contain only the carbohydrate materials and are in a much less objectionable form since their oxygen demand has been reduced to one sixth.

83. Howard, G. C. Lignin derivatives from waste sulfite liquor. U. S. Patent 1,848,292 (Mar. 8, 1932). Original not seen. Abstracted in C. A. 26, 2864 (1932).
Basic calcium lignosulfonate is altered by steam treatment under pressure to yield a material suitable for use as a pigment in rubber or paper products.

84. Howard, G. C. By-products of the Paper Pulp Industry. Chem. Industries 48, 724-26 (1941).
The various types of commercial lignin available and their utilization are discussed.

85. Howard, G. C. and Harmon, C. Dispersions of lignin derivatives. German Patent 605,036 (Nov. 2, 1934). Original not seen. Abstracted in C. A. 29, 1247 (1935).
Calcium lignosulfonates can be treated in the presence of water to produce dispersions which can be used as tanning agents, mordants, dispersing agents, wood preserving agents and insecticides.

86. Jahn, E. C. Utilization of lignin. News Edition, Am. Chem. Soc. 18, 993-6 (1940).
The lignin problem and the present status of its utilization are discussed.

87. Jones, G. W. The chlorination and production of plastics from commercial lignins. Unpublished B. S. Thesis. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa (1941).
Commercial lignins were chlorinated and subsequently reacted with aniline to produce plastic materials.

88. Kalb, L. and Schoeller, V. Cellulose determination by means of phenol. Cellulosechem. 4, 37-40 (1923).
Phenol and small amounts of HCl followed by washing with water and dilute NaOH remove lignin leaving cellulose.

89. Klason, P. Die Lignin Inhalt von Fichtenholz. Cellulosechem. 4, 81-4 (1923).
Klason's method for isolating lignin from wood is described. Spruce wood is treated with 72 per cent sulfuric acid at room temperature and then with boiling 3 per cent sulfuric acid.

90. Klason, P. Constitution of lignin. XII. Ber. 63B, 1548-51 (1930).
Klason suggests that coniferylaldehyde is the building stone for the lignin molecule.

91. Klason, P. Change in lignin content of spruce wood according to climatic conditions. Cellulosechem. 12, 36-37 (1931).
Klason describes his 72 per cent sulfuric acid method for the quantitative estimation of lignin. It is pointed out that the lignin content of spruce wood, regardless of whether from branches or trunk, was remarkably constant. In addition, the age and location of the trees made no difference in the lignin content.

92. König, J. and Rump, E. Chemistry and structure of the vegetable cell membrane. Z. Nahr. Gneussm. 28, 177-222 (1914). Original not seen. Abstracted in C. A. 9, 814 (1915).
König presents evidence in support of the "incrustation hypothesis" concerning the occurrence of lignin in the plant cell.

93. Krings, R. Sulfite waste powder as a raw material for soaps and detergents. Allgem. Oel-U. Fett-Ztg. 34, 192-6 (1937). Original not seen. Abstracted in C. A. 31, 5608 (1937).
"Zewa powder" prepared by drying waste sulfite liquor is described and recommended as an ingredient of soap and detergents. Soap formulas containing this product are presented.

94. Kürschner, K. Sublimation of "unsublimable" substances. Mikrochem. 3, 1-20 (1925).
Various materials, such as pine shavings, pine mold, sulfite liquors, lignite, brown coal, hard coal and lignin separated in various ways from pine, oak, rye straw and red beech wood were subjected to sublimation. In every case crystals of vanillic acid were obtained sometimes mixed with vanillin and NH_4Cl. The vanillic acid is the result of the oxidation of vanillin. Coniferin undergoes the same changes as lignin when sublimed.

95. Kürschner, K. Preparation of larger amounts of vanillin from waste sulfite liquors. J. prakt. Chem. 118, 238-62 (1928).
Details are given of the method and apparatus for heating sulfite waste liquor with KOH in the presence of a stream of air.

96. Kürschner, K. Preparation of vanillin from waste sulfite liquor. Tech. Chem. Papier-u. Zellstoff-Fabr. 30, 1-3 (1933).
Na_2CO_3 is reported as being more economical than Na_2SO_4 and CaO in the treatment of lignin to produce vanillin.

97. Kürschner, K. and Schramek, W. The preparation of vanillin from sulfite waste lignin. Tech. Chem. Papier-u. Zellstoff-Fabr. 28, 65-71 (1931).
The production of vanillin has been studied quantitatively. M-nitrobenzoylhydrazide was used to precipitate the vanillin.

98. Kürschner, K. and Schramek, W. Vanillin from waste sulfite liquor. Tech. Chem. Papier-u. Zellstoff-Fabr. 29, 35-42 (1932).
The optimum conditions for the production of vanillin from sulfite liquor and NaOH are found to be for 4 hours at 6 atmosphere. NaOH can be replaced by Na_2SO_4 and CaO.

99. Lautsch, W., Plankenhorn, E. and Klink, F. The formation of vanillin from wood, lignin and sulfite liquor from fir trees. Angew. Chem. 53, 450-2 (1940).
By use of mild oxidizing agents and the proper reaction conditions, it is possible to decompose lignin containing substances to vanillin. Much larger yields are secured than with previously employed methods. The optimum conditions were determined.

100. Leach, R. W. E. Products such as blocks, sheets, etc., from spent sulfite liquor. U. S. Patent 1,977,728 (Oct. 23, 1934). Original not seen. Abstracted in C. A. 29, 257 (1935).
Ligneous acid resinous constituents are precipitated from spent sulfite liquor. The precipitate is dried and then molded.

101. Liebknecht, O. Ionic-exchange humic materials. Canadian Patent. 373,694 (May 10, 1938). Original not seen. Abstracted in C. A. 32, 5126 (1938).
The ion-exchange power of humic carbonaceous materials is increased by treatment with water at elevated temperatures.

102. Lindsay, F. K. Ion exchangers. Trans. Am. Inst. Chem. Eng. 37, 547-57 (1941).
The inorganic and organic types of ion-exchange materials are reviewed, their capacities compared and their uses surveyed.

103. Loughborough, W. K. and Stamm, A. J. Molecular properties of lignin solutions. J. Phys. Chem. 40, 1113-32 (1936).
Molecular weight studies of lignin separated by various methods range between 4000 and 10,000 as determined from viscosity, osmotic pressure, boiling point raising, diffusion and spreading measurements. The results indicate that lignin is not a chain polymer as is cellulose.

104. McKee, R. H. and Johnston, W. S. Removing fluorides from drinking water. U. S. Patent 2,072,376 (March 2, 1937). Original not seen. Abstracted in C. A. 31, 2723 (1937).
Acidified water containing fluorides is brought into contact with residual carbon such as acid-treated black ash residue from soda-pulp manufacture.

105. Maurer, C. A. The action of nitric acid on lignin. Unpublished B. S. Thesis. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa (1941).
Lignin was nitrated with various concentrations of HNO_3 and mixed acids in a study of the reaction products formed.

106. Mehta, M. M. The nature of lignin. Biochem. J. 19, 958-78 (1925).
Lignin seems to occur in chemical combination with cellulose and related polysaccharides as an aromatic glucoside. Lignocellulose can be separated by treatment with 4 per cent sodium hydroxide at 10 atmospheres for 1 hour.

107. Myers, R. J., Eastes, J. W. and Myers, F. J. Synthetic resins as exchange adsorbents. Ind. Eng. Chem. 33, 697-706 (1941).
The newer synthetic resinous types of cationic and anionic exchange materials are thoroughly discussed and their performance is compared with other types of ionic exchange materials available, both organic and inorganic.

108. National Aluminate Co. Preliminary operating data on Amberlite IR-1 and IR-4. Chicago, Illinois. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa.
The characteristics of the two resinous cationic and anionic exchangers, Amberlite IR-1 and IR-4 are described. Suggested operating data are provided.

109. National Aluminate Co. Use of Nalcite "AX" as a sodium exchanger. Chicago, Illinois. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa.
The operating characteristics of this exchanger are described.

110. Nelson, G. H., Levine, M. and Lynch, D. F. J. Removal of iron by lignin is water treatment. Paper Trade J. 108, No. 9, 29-32 (1939).
Alkali lignin prepared from corncobs was very satisfactory for removing iron from water.

111. Nikitin, N. I. and Rudneva, T. I. The action of chloracetic acid on Willstatter lignin and on wood pulp. J. Applied Chem. (U.S.S.R.) 10, 1915-20 (1937). Original not seen. Abstracted in C. A., 32, 1929 (1938).
Chloracetic acid reacts with lignin to give almost complete solution of the lignin. The lignin in pine wood can be almost completely removed by this same treatment.

112. N. V. Octrooien Maatschappij "Activat." Exchange and adsorptive material. French Patent 784,348 (July 22, 1935). Original not seen. Abstracted in C. A. 30, 256 (1936).
A material having zeolitic properties is made by causing chemical substances, such as SO_3, H_2SO_4, $ZnCl_2$, and H_3PO_4 to react on coal, anthracite, sawdust, peat, lignite, and/or starch.

113. N. V. Octrooien Maatschappij "Activat" and Smit, P. Ion-exchanging substances. British Patent 450,540 (July 14, 1936). Original not seen. Abstracted in C. A. 31, 194 (1937).
Carbonaceous zeolites are obtained by treating anthracite with a current of gaseous SO_3, or a mixture containing it, at not over 250° C.

114. Pauly, H., Foulon, A., Hansen, O., Haberstruh, O., Bailom, H. and Sextl, J. Separation of lignin components. Ber. 67B, 1177-99 (1934).
A study of winter rye straw indicates the presence of at least 5 lignins. Pine lignin gave 8 per cent vanillin when treated with a chromic oxide-sulfuric acid mixture.

115. Payen, A. La composition du tissu propre des plantes et du ligneux. Compt. rend. 7, 1052 (1838).
Woody materials can be fractionated by treatment with nitric acid followed by digestion with potassium hydroxide to dissolve lignin leaving insoluble cellulose.

116. Permutit Co., The. Deacidifying boiler feed water. British Patent 490,704 (Aug. 19, 1938). Original not seen. Abstracted in C. A. 33, 1074 (1939).
The feed water is filtered through a bed of finely divided tanned or untanned skin, fine wool or horn, or albuminous material, the acid-adsorptive properties of which are renewed periodically by treatment with a solution contained hydroxyl ions.

117. Permutit Co., The. Deacidifying liquids. British Patent 490,799 (Aug. 22, 1938). Original not seen. Abstracted in C. A. 33, 1074 (1939).
Aqueous acidic liquids, especially those produced by treating water containing salts with H-ion exchange materials, are deacidified by subjecting them to the action of a basic dye that is insoluble in water and in aqueous acids and alkalies. The salts formed are similarly insoluble and are not hydrolyzed. Suitable dyes are the compounds of the aniline black type obtainable by oxidation of aromatic amines, such as aniline, o-toluidine, etc.

118. Permutit Co., The. Permutit zeolite water softening. Bulletin No. 597. New York. (1939). p. 11-20. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa.
The various classes of base-exchange materials are discussed and their characteristics are described.

119. Phillips, M. Lignin from corn cobs. J. Am. Chem. Soc. 49, 2037-40 (1927).
Lignin was prepared from corn cobs by an alkaline extraction followed by precipitation with acid. A study was made of its chemical and physical properties.

120. Phillips, M. Fractional extraction of lignin from corn cobs. J. Am. Chem. Soc. 50, 1986-9 (1928).
Corn cobs were successively extracted with alcoholic and aqueous sodium hydroxide at various temperatures. The lignin fraction obtained in each step had different methoxyl contents. It is pointed out that part of the lignin is lightly held to the cellulose, as in the case of an ester. The remainder is firmly held as with an ether.

121. Phillips, M. Isolation of n-propylguaiacol as a degradation product of lignin. Science 73, 568-70 (1931).
n-propylguaiacol was in the distillate obtained when lignin was treated with zinc dust at 400° C. in an atmosphere of hydrogen.

122. Phillips, M. The chemistry of lignin. Chem. Reviews 14, 103-70 (1934).
A very excellent and complete review covering the entire subject of lignin and its chemistry.

123. Phillips, M., Goss, M. J., Brown, B. E. and Reid, F. R. The ammoniation of waste sulfite liquor and its possible utilization as a fertilizer material. J. Agr. Res. 53, 209-24 (1936).
The neutralized dry residue of waste sulfite liquor was ammoniated with aqueous NH_3 under pressure to yield a product containing over 10 per cent of N. This material is satisfactory as a fertilizer.

124. Phillips, M. and Weihe, H. Preparation of synthetic resins from alkali lignin. Ind. Eng. Chem. 23, 286-7 (1931).
Aromatic amines and furfural condense with alkali lignins to produce resins. The resins may be used as binders for laminated type structures.

125. Plunguian, M. Preparation and properties of Meadol. Ind. Eng. Chem. 32, 1399-1400 (1940).
Meadol is an alkali lignin precipitated from spent soda black liquor by addition of carbon dioxide. A description of the process is given as well as information on the properties of Meadol.

126. Pomilio, U. Gas chlorination in cellulose manufacture. Ind. Eng. Chem. 31, 657-62 (1939).
A South African plant utilizing straw pines and various native grasses is described. Chlorine and aqueous alkali remove lignin from cellulosic materials.

127. Powell, W. J. and Whittaker, H. Flax lignin and its derivatives. J. Chem. Soc. 125, 357-64 (1924).
Lignin in flax was extracted with sodium hydroxide and subsequently precipitated with hydrochloric acid. Various derivatives were prepared. Evidence is presented showing the existence of phenolic groups in the lignin molecule.

128. Reti, L. Relations among aromatic compounds in plant life and their origin. Atti congresso naz. chim. ind. 250-6 (1924). Original not seen. Abstracted in C. A. 19, 1441 (1925).
A study of the relation in chemical composition among various aromatic compounds occurring in plants indicates that the greater part of the so-called accessory substances represent ramifications of a principal synthesis, the formation of lignin. Vanillin, isoeugenol, guaiacol, protocatechuic acid, gallic acid, the flavones, almost all the anthocyanins and coniferyl derivatives are some of these accessory substances.

129. Riley, R. Zeo-Karb. The Permutit Company. New York, N. Y. (1936). On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa.
The exchange capacity of Zeo-Karb is reported as varying between 11,000 and 13,000 grains per cubic foot when regenerated with varying amounts of salt, and about 15,000 grains per cubic foot when regenerated with acid.

130. Sandborn, L. T. Process of making vanillin. U. S. Patent 2,057,117 (March 28, 1933).
A process is described showing the method of obtaining vanillin from basic calcium lignosulfonate.

131. Sandborn, L. T. Process of making vanillin. U. S. Patent 2,104,701 (March 1, 1937).
Vanillin is extracted directly with butyl alcohol from the alkaline autoclave liquors made from calcium lignosulfonate and sodium hydroxide.

132. Schulze, F. Beitrag zur Kenntniss des Lignins. Chem. Zentr. 28, 321-29 (1857).
Schulze introduced the term lignin into the chemical literature. He used it to describe the material associated with cellulose in plant material. Lignified plant material was oxidized with nitric acid and potassium chlorate.

133. Shearer, K. Vanillin from furfural oat hull residue. Unpublished report. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa. (1942).
Vanillin can be obtained from the oat hull furfural residue when subjected to treatment with an alkaline nitrobenzene mixture.

134. Sherrard, E. C. and Harris, E. E. Factors influencing properties of isolated wood lignin. Ind. Eng. Chem. 24, 103-6 (1932).
The various methods of isolating lignin are compared. Temperature, acid concentration and length of reaction time must be controlled. 70 per cent sulfuric acid at 10° for 16 hours gives best results.

135. Shmuk, A. The chemistry of the organic substances of the soil. Abhandl. Kuban. Landw. Inst. Teil I, Lfg. 2, 1-91 (1923). Original not seen. Abstracted in C. A. 22, 4700 (1928).
The organic substances existing in the soil contain about 14 per cent resinic acids and esters, and about 80 per cent humic acids. The latter is of acid character and contains hydroxyl as well as carboxyl groups. The ash is not bound organically. Analysis on ash free basis gave C-61.8 per cent, H-4.2 per cent and N-3.2 per cent. N is present in the form of ordinary protein compounds.

136. Shorigan, P. P. and Smolyaninova, E. K. The production of vanillin from wood and sulfite liquors. J. Gen. Chem. (U.S.S.R.) 4, 1428-33 (1934). Original not seen. Abstracted in C. A. 29, 3665 (1935).
The precipitation of vanillin with the m-nitrobenzoylhydrazine is superior to other reagents, e.g., sodium bisulfite and hydroxylamine. Modifications of Kurschner's method are presented.

137. Skinner, H. J. Waste problems in the pulp and paper industry. Ind. Eng. Chem. 31, 1331-35 (1939).
The outstanding wastes which cause stream pollution are waste sulfite liquor and fiber wastes. The Howard process is described. Uses of lignin are described.

138. Smyser, F. H. Molded products from cellulosic material. U. S. Patent 1,792,254 (Feb. 10, 1931). Original not seen. Abstracted in C. A. 25, 1993 (1931).
A cellulosic material such as sawdust, bagasse or cornstalks having natural substances capable of yielding resinous compounds is digested with NaOH, and H_2SO_4 is added to the digested mass to precipitate the dissolved resinous constituents. The material is powdered and is molded under heat and pressure.

139. Throhdal, M. C. Studies in the degradation of lignin by caustic fusion. Unpublished M. S. thesis. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa. (1941).
A study of the caustic fusion of lignin was made in an effort to obtain various polyhydric phenolic materials.

140. Tiger, H. L. Determining the quality of zeolites. J. Am. W. W. Assoc. 26, 357-70 (1934).
Methods of determining the quality of inorganic zeolites are given.

141. Tiger, H. L. Carbonaceous zeolites. Trans. Am. Soc. Mech. Eng. 60, 316-325 (1938).
The new hydrogen zeolites not only remove calcium and magnesium alkalinity, but also remove sodium alkalinity. Since they are carbonaceous in nature, they are practically free of silica and thus may be used with waters of low ph.

142. Tiger, H. L. and Goetz, F. C. Stabilizing base-exchange humates. U. S. Patent 2,069,564 (Feb. 2, 1937).
Granules of humic acid base-exchange materials are digested in a saline solution containing chromic oxide. This treatment tends to eliminate discoloration of water softened by the above material.

143. Tomlinson, G. H. and Hibbert, H. The formation of vanillin from waste sulfite liquor. J. Am. Chem. Soc. 58, 345-8 (1936).
The formation of vanillin by the action of hot alkalies or waste sulfite liquor was confirmed and a satisfactory method developed for its estimation and quantitative extraction from the reaction mixture.

144. Tomlinson, G. H. and Hibbert, H. Mechanism of vanillin formation from spruce lignosulfonic acids in relation to lignin structure. J. Am. Chem. Soc. 58, 348-53 (1936).
Evidence is presented to show the relation between the sulfonic acid group of the lignosulfonic acids and vanillin formation.

145. United Water Softeners, Ltd. Ion-exchange material. British Patent 450,574 (July 21, 1936). Original not seen. Abstracted in C. A. 31, 493 (1937).
Carbonaceous zeolites are obtained by treating vegetable matter, e.g., peat, lignite and anthracite with strong sulfuric acid, the reaction being terminated before there is any appreciable formation of free carbon.

146. United Water Softeners, Ltd. Base-exchange substances. British Patent 451,899 (Aug. 13, 1936). Original not seen. Abstracted in C. A. 31, 494 (1937).
Treatment of base-exchange substances containing humic acid with a solution of chromium combined as a base is effective in overcoming discoloration of water softened by the above type of substances.

147. Urbain, O. M. and Stemen, W. R. Preparing coal for use in water purification. U. S. Patent 2,137,932 (Nov. 22, 1938). Original not seen. Abstracted in C. A. 33, 1849 (1939).
Absorptive material may be prepared by passing Cl_2 through powdered coal to form a product rich in combined chlorine. This is the hydroxylated by treatment with steam or similar hydroxyl-containing materials.

148. Wallace, F. J. Condensation products from sulfite waste liquor, phenol and aldehyde. U. S. Patent 2,159,411 (May 23, 1939). Original not seen. Abstracted in C. A. 33, 6993 (1939).
A process for the manufacture of condensation products from the solids of sulfite waste liquor by mixing together the waste liquor, a phenolic compound and HCHO. These materials are heated until they react to form a composite resinous body, which is suitable for coating, insulation, etc.

149. Walseth, C. S. Studies on the dye possibilities of lignin derivatives. Unpublished B. S. thesis. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa. (1941).
Azo dyes were prepared by nitrating lignin, reducing it, then diazotizing and finally coupling to various intermediates.

150. Wassenegger, H., Griessbach, R. and Sutterlin, W. Water insoluble cation exchange. U. S. Patent 2,228,159 (Jan. 7, 1941). Original not seen. Abstracted in C. A. 35, 2653 (1941).
A phenol-formaldehyde condensation product is treated during its formation with an aqueous solution of an alkali sulfite in the presence of CH_2O at a temperature up to the boiling point. Heating is continued until the mass solidifies to a gel, and this is dried at about 80°.

151. Wassenegger, H. and Jaeger, K. Effective cation exchange, as in removing calcium from hard waters. U. S. Patent 2,204,639 (June 11, 1940). Original not seen. Abstracted in C. A. 34, 7049 (1940).
In treating aqueous solutions for cation exchange, use is made of a water insoluble resin formed from an aldehyde and a solfonic acid of hydroxybenzene, naphthalene, acenaphthene or phenanthrene. Various examples with details are given.

152. Way, J. T. On the power of soils to absorb manure. J. Royal. Agri. Soc. 11, 313-379 (1850).
Sand from soils does not retain ammonia. The clayey constituents of soil are the active agents that retain basic ions of salts of ammonia, potassium, magnesium, calcium and sodium.

153. Way, J. T. Power of soils to absorb manure. J. Royal Agri. Soc. 13, 123-243 (1852).
Base-exchange is chemical. Replaced ions are quantitatively exchanged for calcium. A material with properties similar to that of soils was prepared by the reaction of aqueous solutions of sodium aluminate and sodium silicate.

154. Wenzel, H. The isolation of lignin with a mixture of phosphoric and hydrochloric acids. Cellulosechem. 7, 88-9 (1926).
A mixture of phosphoric acid (sp. gr. 1.7) and hydrochloric acid (sp. gr. 1.18) is used for the isolation of lignin.

155. Wharton, R. H. Azo dyes from ammoniated lignin. Unpublished B. S. thesis. On file. Department of Chemical Engineering, Iowa State College, Ames, Iowa. (1942).
Efforts were made to prepare azo dyes from ammoniated lignin, diazotizing this and then coupling to various intermediates.

156. Williams, V. V. and Rafanova, R. Y. Vanillin from sulfite waste liquor. Russian Patent 51,796 (Sept. 30, 1937). Original not seen. Abstracted in C. A. 33, 9644 (1939).
Sulfite waste liquor is acidified and the solution separated from the precipitate. Vanillin is extracted from the solution with an organic solvent, the solvent is then evaporated and the residue is heated with H_2O to remove the resins. The vanillin is recovered from the aqueous solution by extraction with an organic solvent.

157. Willstätter, R. and Zechmeister, L. Zur Kenntnis der Hydrolyse von Cellulose. Ber. 46, 2401-12 (1913).
Fuming hydrochloric acid, density 1.212 to 1.223 at 15° C., will completely hydrolyze cellulose in the cold. A quantitative method for the determination of lignin in wood can be based on this treatment.

158. Wislicenus, H. Colloid chemistry of the synthesis and degradation of the cellulose framework of the plant, "lignin" and wood fiber. Cellulosechem. 6, 45-58 (1925).
Lignin is a heterogeneous mixture deposited primarily by adsorption, later by colloidal aggregation on the surface of the cellulose fiber.

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